PB88-234067

Development and Evaluation of Composite Receptor Methods

Environmental Protection Agency
Research Triangle Park, NC

Jul 88

U.S. Department of Commerce
National Technical Information Service
NTIS

PB88-234067

EPA/600/3-88/026
July 1988

DEVELOPMENT AND EVALUATION OF COMPOSITE RECEPTOR METHODS

by

Thomas G. Dzubay
Atmospheric Sciences Research Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-88/026	2.
3. RECIPIENT'S ACCESSION NO. PB88 234067/AS	
4. TITLE AND SUBTITLE DEVELOPMENT AND EVALUATION OF COMPOSITE RECEPTOR METHODS	5. REPORT DATE July 1988
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T.G. Dzubay	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO. A101/B/67/01-2310 (FY-88) 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

A composite receptor method for PM-10 apportionment was evaluated to determine the stability of its solutions and to devise cost-effective measurement strategies. Aerosol samples used in the evaluation were collected during summer, 1982, by dichotomous samplers at three sites in the vicinity of Philadelphia, PA. The composite receptor method consisted of a wind-trajectory method, chemical mass balance (CMB), and multiple linear regression (MLR). Several industrial sources were determined by CMB, and vehicle exhaust and a sulfur-component were determined by MLR. Measured Pb minus a CMB-derived correction for other sources was used as an independent variable in MLR, and MLR results for the Pb abundance in vehicle exhaust agreed with predictions of a model for vehicle emission factors. In resolving PM-10 into 11 components, scanning electron microscopy was essential for coal-fly ash and botanical matter, x-ray fluorescence (XRF) was needed for the sulfur-component and vehicle exhaust, and instrumental neutron activation analysis (INAA) was essential for fluidized catalytic crackers at refineries. The remaining components were determined well by either INAA or XRF. Ten to twenty samples were sufficient to determine average source contributions by CMB. At least 50 samples were needed to determine vehicle exhaust and the sulfur-component by MLR.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 63 22. PRICE PC $14.95 / MF $6.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

ACKNOWLEDGEMENTS

The author thanks Robert Stevens for encouragement and valuable discussions throughout this study, Glen Gordon, Ilhan Olmez and Ann Sheffield for sample analysis by instrumental neutron activation and for valuable discussions, Al Thompson and Joseph Jaklevic for x-ray diffraction analysis, Yaacov Mamane and John Miller for scanning electron microscopy analysis, William Courtney, George Russwurm, William Ellenson, Charles Tipton, Carolyn Owen, Chris Pressley, Mark Mason and Margaret Beaman for all other sample analyses, and James Godowitch for providing hourly wind data.

DISCLAIMER

The information in this document has been funded by the United States Environmental Protection Agency. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of commercial products does not constitute endorsement by U. S. EPA.

CONTENTS

Acknowledgment ii

1. Introduction 1

2. Conclusions and Recommendations 3

3. Measurements 5
   - Procedures 5
   - Precision and accuracy 6
   - Ionic composition 8
   - Crystalline Species Measured by X-Ray Powder Diffraction 10

4. Results and Discussion 13
   - Composite method description and results 13
   - Evaluation of composite receptor method 20
   - Cost-effective strategy for sampling and analysis 32

References 33

Appendices

A. Example of typical data stored on diskette 37

B. X-ray powder diffraction results..... 38

C. Source signatures for fine particles 44

D. Source signatures for coarse particles 46

E. Fine particle CMBs for individual samples at site 28 48

F. Coarse particle CMBs for individual samples at site 28 49

G. Example of results of MLR analysis..... 50

H Printout for EPA CMB code applied to fine particles at site 28 53

I. Annotated printouts of model for particulate vehicle emissions 55

TABLES

1 Summary of ambient aerosol measurements 6

2 Aerosol composition at site 28 in Camden, NJ 7

3 Comparison of XRF and INAA results 8

4 Comparison of XRF and IC results for sulfur 9

5 XPD results for fine particles at site 28 11

6 XPD results for coarse particle at site 28 12

7 Aerosol composition for events selected by wind-trajectory method ...14

8 Fine-particle CMB for average composition at site 28 15

9 Coarse-particle CMB for average composition at site 28 16

10 Results of composite receptor method 17

11 Multiple linear regression results by site 18

12 Scanning electron microscopy results for site 28 19

13 Dependence of fine fraction CMB on source signatures 21

14 Dependence of coarse fraction CMB on source signatures 22

15 Effect of measurement method on mass apportionment 24

16 Multiple linear regression results for various data subsets 25

17 Effect of measurement method on MLR results 26

18 Lead abundance in 1982 vehicle emissions predicted by model 27

19 Lead abundance in 1982 vehicle emissions derived by MLR 28

FIGURES

1 Map showing locations of sampling sites and emission sources 2

2 Model results for VMT-weighted Pb emission rate from vehicles 29

3 Model results and MLR results for Pb abundance in vehicle exhaust ...29

4 Modified dichotomous sampler suitable for both SEM and bulk sample analysis 31

SECTION 1

INTRODUCTION

Receptor models are techniques for using data on the composition of atmospheric aerosol to resolve particulate mass concentration into components related to emission sources[1-3]. The U. S. Environmental Protection Agency has specified that receptor models may be used with dispersion models to develop plans to meet its new PM-10 standard[4]. The Agency has developed guidelines on how the chemical mass balance (CMB) receptor model is to be used[5-7]. The present report explores how the resolution and accuracy of the CMB model can be improved by using CMB in conjunction with other receptor methods and by using measurement data by a variety of methods such as x-ray fluorescence (XRF), instrumental neutron activation (INAA), scanning electron microscopy (SEM), and x-ray powder diffraction (XPD).

This report is based on data obtained in a study intended to develop and improve the capabilities of receptor models[8]. The study was designed according to recommendations from the Quail Roost II Conference[9]. Ambient aerosol was collected in the PM-10 size range (particle diam $\leq$ 10 μm) at three sites in the Philadelphia area during summer, 1982[8]. Figure 1 shows locations of sampling sites and major emission sources. Source emissions were collected using a dilution-cooling technique at two oil-fired power plants, a coal-fired power plant, a municipal incinerator, an Sb ore roaster, a fluidized catalytic cracker at a refinery, and a secondary Al smelter[10]. Surface soil and dust were collected at 30 sites and suspended by an aerosol generator[11]. Ambient, source, and soil samples were collected by dichotomous samplers and analyzed by XRF, INAA, ion chromatography (IC), pyrolysis, SEM and XPD.

The Philadelphia study led to the development of a composite receptor method that uses several different receptor methods in concert[8]. The composite method was developed to overcome limitations that those receptor models have when used individually. It includes a wind-trajectory method[12] to identify significant sources of trace elements, CMB to determine their contributions to PM-10, and CMB combined with multiple linear regression (MLR) to determine vehicle exhaust and a sulfur-component[8]. The latter consists of particles containing sulfate, related cations and possibly water and carbon.

In developing the composite method, it was recognized that three criteria must be met for a species to be included in a CMB:

(1) All sources of the species must be included in the CMB.
(2) The species' abundance in particulate emissions from all of those sources must be known.
(3) Sources with collinear signatures (i. e. similar species abundances) cannot be determined individually and must be included in a broadly defined source category.

Signature data have been compiled for more than 120 sources[13], and many might be applicable to Philadelphia. However, collinearity becomes severe in a typical CMB if more than 6 to 12 components are included. Thus, the wind

trajectory method[12] was valuable for selecting sources to include in CMB analyses. Components in CMBs for fine particles were crustal matter and emissions from municipal incinerators, oil-fired power plants, fluidized catalytic cracker, antimony roaster, and paint pigment manufacturing. Because signatures for coal-fly ash and soil were collinear, criterion 3 required that they be included in a broadly defined crustal source category. Elements included in CMB analyses were Si, Ti, Fe, Ni, Zn, Cd, Sn and Sb measured by XRF and Al, V, La, Ce and Sm measured by INAA[8].

Criterion 2 led to the exclusion of Pb and S from the CMB because their abundances were not known well for vehicle exhaust and a sulfur-component. The latter consisted of sulfate, cations and possibly water or organic matter. Multiple linear regression (MLR) can be used to estimate S- and Pb-abundances, but measured Pb could not be used as an independent variable in MLR because vehicle exhaust was not the only significant source of Pb. Thus, the above described CMB was applied to each ambient sample to determine non vehicular Pb, which was subtracted from measured Pb to yield a vehicle-exhaust tracer. This work describes application of MLR to various data subsets chosen to reveal any dependence on sampling site, sample size and measurement method.

Apportionments presented here include SEM results for botanical matter and coal-fly ash in coarse particles[14,15]. SEM provided estimates for several other components including emissions from municipal incinerators[15]. For samples heavily impacted by municipal incinerators, SEM confirmed CMB results. However, cases were identified where CMB results indicated municipal incinerator emissions when none was detected by SEM[15]. Evaluation of those cases suggested possible departure from criterion 1 because Zn, an important tracer for incinerators, had other possible sources not included in the CMB. Thus, this work includes an evaluation to determine the effect of cases with high Zn concentrations on the results of the composite receptor method.

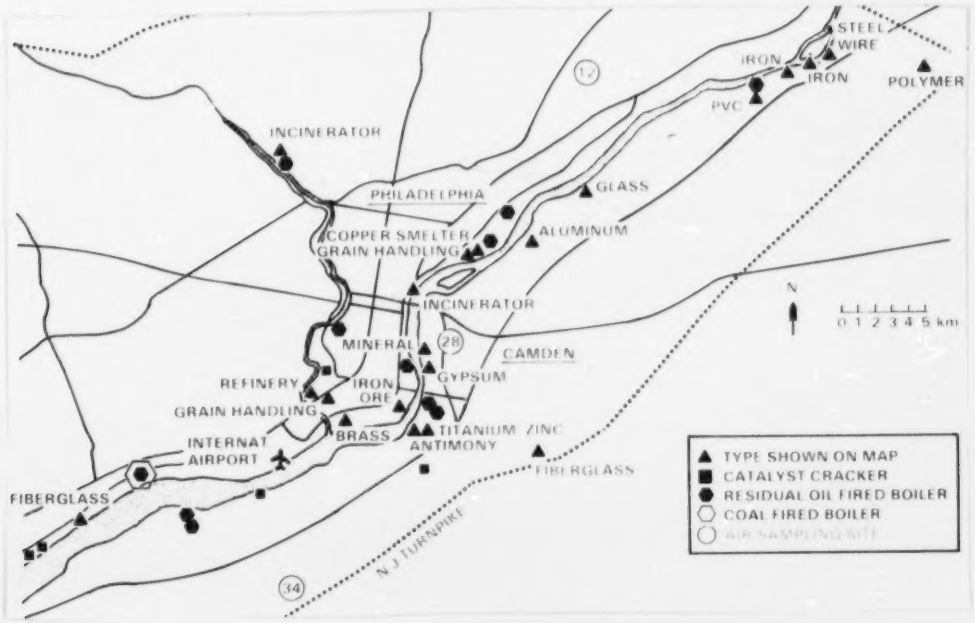

Figure 1. Map showing locations of sampling sites and emission sources.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

A new composite receptor method that combines wind trajectory analysis, CMB and MLR was applied to data obtained by XRF, INAA and SEM. The combined use of XRF and INAA enabled more sources to be resolved than was possible when only one method was used. The former provided essential data on Si, S, Ni, and Pb; the latter provided essential data on Al, V, Se, La, Cs, and Sm. Although INAA was applied only to samples in the fine fraction, coarse particle INAA data for Na would have been helpful for improving the accuracy of the marine component. The wind-trajectory method identified five categories of stationary sources to include in the CMB. Perhaps more sources could have been identified if sampling periods had been shorter than 12 hours.

The composite method enabled PM-10 to be resolved into 11 components. The method provided an estimate of the average Pb abundance in vehicle exhaust when incinerators and oil combustion contributed a portion of the Pb. Final results indicate that the vehicle exhaust portion of PM-10 ranged from 6% to 12%. Stationary sources included in our CMB contributed less than 5% to PM-10. The sulfate component contributed 54 ± 10% of PM-10 and consisted of sulfate plus related water and ions. Wind-stratified data indicated that 80 ± 20% of particulate S was from regional sources beyond the Philadelphia area. Regression of S vs tracers Se and either V or Ni attributed 72 ± 8 and 16 ± 5% of particulate S to coal- and oil-fired power plants, respectively.

XRF data were essential for obtaining accurate determinations of a large sulfur-component and vehicle exhaust. INAA was essential for determining a 0.2 $\mu g/m^3$ contribution by fluid catalytic crackers at refineries. Coarse particles were not analyzed by INAA, but INAA data for Na would have been helpful to determine the marine component. SEM was essential for determining 0.2 and 2 $\mu g/m^3$ contributions of coal-fly ash and botanical matter, respectively. Remaining components were determined well by either INAA or XRF data. Is it worth the cost of obtaining INAA and SEM data to determine such small components as was found in this study for catalytic crackers and coal-fly ash? To answer that question, one must weigh the cost of INAA and SEM measurements against the cost of requiring control measures for sources whose contributions to PM-10 are unknown.

Evaluation of data for 156 samples suggests a more economical and effective design for PM-10 apportionment in the Philadelphia study. Because INAA and SEM-EDX data were not directly used in MLR, it was only necessary to analyze enough samples to provide adequate estimates of the means. Standard errors computed from the standard deviations of CMB-derived component concentrations suggest that 10 to 20 randomly selected samples analyzed by INAA and SEM-EDX should be sufficient for major species. However, it is appropriate that all samples were analyzed by XRF because XRF analysis is less expensive and many analyzed samples were needed for the composite of CMB and MLR. Analysis of data subsets by MLR indicates that the sulfur-component was

determined well with as few as 31 samples, but the vehicle-component required more than 50 samples.

Analysis of sulfate collected in dichotomous samplers was of little value in the present study other than to confirm that XRF could be used to measure S in sulfate. In future studies, it would be more useful to collect samples with annular denuder systems so that the nitrate volatilization problem car be avoided and both gaseous and particulate S and N compounds can be analyzed.

In the Philadelphia study, two dichotomous samplers were used to collect samples for XRF and SEM analyses. The use of two dichotomous samplers is not only expensive, but the resulting fine fraction samples are unsuitable for analysis by SEM. The modified dichotomous sampler shown in this report provides a way to use one device to collect both fine and coarse particles that can be analyzed by XRF, INAA and SEM.

The abundance of S in the sulfur-component derived by CMB-MLR was at least 19% lower than that of S in pure sulfate salts. Measurement error can account for no more than half of the difference. Much of the difference may be due to water or carbon bound to sulfate particles.

If Pb is used as a tracer to determine vehicle exhaust by CMB analysis, the average Pb abundance in emissions from the entire fleet of vehicles needs to be determined. In the present study, it was shown that the abundance of Pb in vehicle exhaust could be derived by CMB-MLR, and the results agreed with predictions of a comprehensive emissions model for vehicle emissions. If the model and its parameters were fully validated, it could be used instead of an expensive set of field measurements to derive the Pb abundance. However, not all parameters in that model have been validated, and the model does not include particulate mass resulting from condensation of exhaust gasses in the atmosphere. Until the model is validated for use with CMB, a composite of CMB and MLR will be needed to determine the Pb abundance.

Decreasing use of Pb in fuel will make it difficult to use Pb as a tracer for vehicle exhaust in future years. The model for motor vehicle exhaust predicts a factor of 20 decrease in Pb-emission rate between 1982 and 1990. Most of the decrease occurred between 1984 and 1986 when the Pb content of gasoline in the United States decreased by a factor of 11. Such decreases imply that if the measurements described in this report were repeated in 1990, vehicles would contribute only 20% of ambient Pb in Camden, NJ. Such a low vehicle contribution will be a difficult challenge even for the composite of MLR and CMB. One way to overcome this difficulty might be to use the composite of CMB and MLR to deduce the Pb abundance in vehicle exhaust sampled near a roadway. Because Pb emission rates differ widely among various classes of vehicles, it is important that the roadway sampling site represents the vehicle mix and driving speeds of areas where PM-10 is to be apportioned.

An alternative would be to use another tracer for vehicles. A tendency for Br to volatilize in the presence of acid aerosol makes Br a tracer of questionable quality. Carbon monoxide may be a better one, but, in future years, as the proportion of vehicles with control devices for CO increases, non vehicular sources of CO are likely to interfere with CO from vehicles.

SECTION 3

MEASUREMENTS

PROCEDURES

Ambient aerosol samples were collected nearly continuously at three sites shown in Figure 1 for 12-h periods during day (0600-1800 EDT) and night (1800-0600) between July 14 and August 13, 1982. Site 28, at the Institute for Medical Research in Camden, NJ, was in an industrial, commercial area within 10 km of several large emission sources (Figure 1) and was within 400 to 500 m of several major roads. Site 12, at Northeast Airport, was in a residential area of Philadelphia with isolated light industrial parks; the closest major road was 500 m to the south. Site 34, at Shady Lane Rest Home near Clarksboro, NJ, was in a rural area 1 km northwest of the New Jersey Turnpike. Emission sources in the area are described by Core[16].

Automated dichotomous samplers (Beckman Instruments) were used to collect fine (<2.5-μm aerodynamic diam) and coarse (2.5- to 10-μm) particles on 2-μm pore size Teflon filters at all three sites. Dichotomous samplers were also used to collect particles on quartz filters (Type 2500 QAST quartz, Pallflex Corp.) at Sites 12 and 28. Efficiencies for 0.035 to 1 μm particles were >99.9% for Teflon and ≥91% for quartz[17]. To improve adhesion, the Teflon filters used to collect coarse particles were coated with 25 $\mu g/cm^2$ of mineral oil before determining tare masses[18]. The inlets were prototypes of a PM-10 inlet now available from Sierra-Andersen, Inc. Flow rates, set at 1 m^3/h, were measured every 5 days using a dry-gas test meter and were constant within 4%. At the end of the study, flow rates were checked by an auditor; deviations ranged from 0 to 12%, and the average was 5%.

Additional samples on Teflon filters were collected for x-ray powder diffraction analysis (XPD) using dichotomous samplers developed by Lawrence Berkeley Laboratory for use in the Regional Air Pollution Study[19]. Flow rates of 1 m^3/h were used to collect heavily loaded samples required for XPD. Samples were analyzed by XPD at Lawrence Berkeley Laboratory[20-21], and results were provided by Thompson and Jaklevic (private communication).

Teflon filters were analyzed for mass by β-ray attenuation[22-23] in a RH ≈ 50% laboratory atmosphere and for elemental composition by an energy dispersive XRF spectrometer having Ti, Mo and Sm secondary targets[19]. Fine fraction filters were sent to the University of Maryland for analysis by INAA using the National Bureau of Standards' heavy water reactor[24]. Pyrolysis of 0.35-cm^2 portions of quartz filters was used to determine volatilizable carbon (V-C) (650°C in a He atmosphere) and non-volatilizable carbon (NV-C) (850°C in a 98% He, 2% O atmosphere)[25]. The remainder of each quartz filter was analyzed for sulfate and nitrate by IC and for ammonium by colorimetry[26,27].

Table 1 provides a summary of ambient aerosol measurements. Data for mass, elemental concentrations, ionic species and carbon were merged into a single record for each sampling period, and Appendix A illustrates a typical one. The data set consists of 157 records for 52, 51, and 54 samples at sites 12, 28 and 34, respectively. The data are stored on a diskette readable by an IBM PC, and copies may be obtained from the author of this report.

When species concentrations are below an instrument's detection limit, negative concentrations are often obtained. Although such data have no physical meaning, they represent valid data in the statistical population of results. It is tempting to delete negative results, but to do so introduces bias, which the following example illustrates: Suppose that the true concentration of a species is zero, and it is measured many times with an instrument that has finite precision and zero bias. Positive and negative measurement results are equally probable, and the average for all measurements is expected to be zero. However, if the negative data are deleted, the average concentration will be positive, which is a biased result. Thus, negative XRF and ionic species data were not deleted in this study.

TABLE 1. SUMMARY OF AMBIENT AEROSOL MEASUREMENTS

Site	Flow rate, m^3/hr	Filter type	Number* F	Number* C	Measurement method	Reference
12	1	Teflon	52	52	β-gauge, XRF, INAA	8
12	1	Quartz	59	59	IC, pyrolysis	8
12	3	Teflon	29	46	β-gauge, XRF, XPD	22
12	1	Nuclepore/Teflon+	53	53	β-gauge, XRF	
			3	5	SEM-EDX	14,15
28	1	Teflon	51	51	β-gauge, XRF, INAA	8
28	1	Quartz	60	60	IC, pyrolysis	8
28	3	Teflon	25	46	β-gauge, XRF, XPD	22
28	1	Nuclepore/Teflon+	53	53	β-gauge, XRF	
			3	7	SEM-EDX	14,15
34	1	Teflon	54	54	β-gauge, XRF, INAA	8

*Number of samples analyzed in fine (F) and coarse (C) fractions.
+For samples collected in August, Nuclepore filters were used for both size fractions. For samples collected in July, Nuclepore was used for coarse fraction, and Teflon was used for the fine fraction.

PRECISION AND ACCURACY

Systematic errors were ±7% for sulfate by IC, ±11% for Al by XRF, and ±7% for other elements by XRF. Errors for INAA were the larger of either ±10% or random error determined from counting statistics. For each measured species, Table 2 lists mean and maximum concentration, mean uncertainty, and the number of samples having concentration above twice the uncertainty. Variability in blank samples resulted in large uncertainty for V-C. Table 2 is based on the 50 sampling pe iods for which there were complete data for all measuring methods. (For one period, data were not available by all methods at site 28.)

TABLE 2. AEROSOL COMPOSITION AT SITE 28 IN CAMDEN, NJ[+,*].

	Fine fraction				Coarse fraction			
	Method	N	Average	Max.	Method	N	Average	Max.
mass	β-gauge	49	28712 (3124)	64309	β-gauge	43	11433 (2793)	24757
NO_3^-	IC	3	132 (161)	635	IC	37	573 (166)	1594
SO_4	IC	50	11156 (858)	31369	IC	23	521 (304)	2449
NH4	colorim.	49	3601 (274)	11242	colorim.	0	-268 (84)	142
V-C	pyrolysis	25	2046 (1014)	5806	pyrolysis	1	620 (1002)	2656
NV-C	pyrolysis	50	1867 (142)	4190	pyrolysis	40	416 (60)	1700
Na	INAA	50	146 (15)	936				
Al	INAA	50	53 (6)	139	XRF	49	549 (169)	2328
Si	XRF	50	103 (21)	215	XRF	50	1613 (387)	5017
S	XRF	50	4196 (287)	10712	XRF	50	230 (139)	668
Cl	XRF	3	3 (5)	443	XRF	41	69 (13)	1380
K	XRF	49	101 (8)	897	XRF	50	151 (23)	300
Ca	XRF	50	40 (5)	82	XRF	50	363 (37)	894
Sc *	INAA	50	14 (2)	35				
Ti	XRF	19	15 (9)	98	XRF	36	65 (12)	172
V	INAA	50	13 (1.4)	41	XRF	25	7 (4)	27
Cr	INAA	49	1.5 (0.2)	8	XRF	13	3 (3)	52
Mn	INAA	50	6 (0.7)	12	XRF	44	11 (3)	41
Fe	XRF	50	91 (7)	263	XRF	50	493 (37)	1218
Co *	INAA	50	483 (63)	1942				
Ni	XRF	46	11 (1.5)	39	XRF	33	4 (1)	18
Cu	XRF	15	1 (2)	16	XRF	11	1 (2)	35
Zn	XRF	50	82 (6)	876	XRF	47	30 (4)	154
Ga *	INAA	16	76 (84)	475				
As *	INAA	49	632 (215)	3399				
Se *	INAA	50	1764 (210)	4929	XRF	2	0.0 (0.5)	0.8
Br	XRF	50	29 (2)	82	XRF	50	15 (1.4)	37
Sr	XRF	10	0.4 (0.6)	2	XRF	39	2 (0.6)	7
Mo *	INAA	38	880 (360)	4317				
Ag *	INAA	18	167 (120)	1921				
Cd	INAA	24	2.2 (0.7)	21	XRF	1	0 (2)	7
In *	INAA	12	7 (4)	89				
Sn	XRF	9	5 (4)	55	XRF	3	1 (3)	10
Sb	INAA	50	79 (8)	1155	XRF	3	181 (13)	2670
I *	INAA	46	1039 (316)	2829				
Cs *	INAA	23	23 (14)	179				
La *	INAA	50	1324 (148)	11300				
Ce *	INAA	45	610 (97)	3832				
Sm *	INAA	50	40 (5)	178				
W *	INAA	34	227 (60)	2037				
Au *	INAA	27	1.7 (0.9)	11				
Pb	XRF	50	249 (15)	837	XRF	50	54 (5)	134

[+] For 50 samples, N is the number having concentration above 2 times the uncertainty. Data in parentheses represent mean uncertainties. Data represent the period from July 14 to August 13, 1982

[*] An asterisk (*) denotes data in pg/m^3; all other data are in ng/m^3.

Table 3 shows a comparison of XRF and INAA results for 10 species that have mean concentrations above random error δ. The ratios of means agree within overall error estimates for S, Ca, Mn, Fe, Zn, and Sb.

TABLE 3. COMPARISON OF XRF AND INAA RESULTS FOR 50 PAIRED FINE PARTICLE MEASUREMENTS AT SITE 28*

	XRF, ng/m³		INAA, ng/m³		Ratio of means (XRF/INAA)	R
	Mean	δ	Mean	δ		
S	4196	20	3863	700	1.09 ± 0.21	0.92
K	101	3	144	12	0.70 ± 0.13	0.94
Ca	40	5	49	18	0.81 ± 0.22	0.65
V	19	4	13	0.6	1.43 ± 0.18	0.86
Mn	6	2.3	6	0.3	1.09 ± 0.15	0.72
Fe	91	3	94	10	0.97 ± 0.12	0.89
Zn	82	1.5	92	5	0.89 ± 0.11	0.997
Se	1.2	0.6	1.8	0.1	0.67 ± 0.10	0.70
Br	29	0.8	23	0.3	1.27 ± 0.16	0.97
Sb	73	5	79	4	0.93 ± 0.11	0.998

*R is the correlation coefficient. δ is the typical amount of random error in individual measurements having concentrations similar to the mean. The uncertainties in the ratio include random error for N=50 and systematic error.

IONIC COMPOSITION

Ammonium and sulfate were highly correlated (R = 0.97). The NH_4^+/SO_4^{2-} molar ratios were 1.51 ± 0.11 and 1.72 ± 0.12 for Sites 12 and 28, respectively. Data in Table 2 indicate that any Na, K, Ca, Fe and Pb cations would contribute <8% of the anion/sulfate molar ratio. If the remaining amount of anion was H^+, the H^+/SO_4^{2-} molar ratio was 0.4 ± 0.2. Such a value is a lower limit for H^+ because samples were not protected from neutralization by NH_3 during 1 to 14 days of storage in dichotomous samplers.

Table 2 indicates significant negative bias for coarse particle ammonium, which is explained as follows: the dichotomous sampler deposits 10% of the fine particles on the coarse-fraction filter where $(NH_4)_2SO_4$ in fine particles may contact alkaline coarse particles, causing the former to decompose and lose NH_3. When computing species concentrations, a mathematical correction[27] for fine particles deposited on the coarse fraction filter was made assuming zero loss; thus, any loss would cause negative bias.

Nitrate data reported here pertain to nonvolatilized nitrate. Ammonium nitrate is unstable, and the more stable alkaline nitrate compounds may decompose upon contact with acidic fine particles after collection on a filter. Thus, little nitrate was detected in the fine fraction. Most nitrate was collected in the coarse fraction where alkaline minerals are abundant and can react with gaseous HNO_3 to form stable nitrate salts. (XPD data for minerals are presented in the next section.) Little nitrate was detected in source[10] or soil[11] samples, which suggests that coarse particle nitrate was

produced by reactions between particles and HNO_3 in the atmosphere. Such reactions could not have happened on the filter because metal tube walls upstream of the filters in a dichotomous sampler remove nitric acid[28]. In future studies it would be useful to collect samples with annular denuder systems so that the nitrate volatilization problem can be avoided, and both gaseous and particulate S and N compounds can be analyzed[29].

Table 4 shows a comparison between IC measurements of SO_4^{2-} (expressed as S) and XRF measurements of S in fine particles. Results indicate that XRF and IC data for fine particle S are highly correlated, and the means agree within measurement error. Because IC detected only sulfate, it is concluded that within measurement error, all S occurred as sulfate in the fine fraction. Table 4 shows that when two outliers out of 102 measurements are deleted, the correlation improves slightly.

TABLE 4. COMPARISON OF XRF DATA FOR S AND IC DATA FOR SO_4^{2+} EXPRESSED AS S*

Site	12	28	12 & 28	12 & 28#
Number of paired samples analyzed	51	50	101	99#
Max. S conc. measured by XRF, μg/m³	11.79	10.71	11.79	11.79
Max. S conc. measured by IC, μg/m³	11.62	10.46	11.62	11.62
Mean S conc. measured by XRF, μg/m³	3.93	4.06	4.00	3.99
Mean S conc. measured by IC, μg/m³	3.66	3.72	3.69	3.72
Ratio of means (XRF/IC)	1.07 ± 0.09	1.09 ± 0.09	1.08 ± 0.09	1.07 ± 0.09
Correlation Coefficient R	0.987	0.974	0.981	0.992
Intercept A, μg/m³	0.41 ± 0.10	0.41 ± 0.15	0.41 ± 0.09	0.37 ± 0.06
Slope B	0.960 ± 0.022	0.981 ± 0.033	0.971 ± 0.019	0.972 ± 0.013

*Slope and intercept pertain to the relationship, [XRF] = A + B [IC], where the quantity in brackets is the S concentration measured by the indicated method.

#Two outliers are removed.

CRYSTALLINE SPECIES MEASURED BY X-RAY POWDER DIFFRACTION (XPD)

Tables 5 and 6 show typical results of XPD analyses for samples from site 28. Additional typical XPD results are in Appendix B. These results were provided by Jaklevic and Thompson of Lawrence Berkeley Laboratory, (private communication).

In the fine fraction, S was measured by XPD as mainly mascagnite, which is ammonium sulfate, and XRF and XPD measurements for S generally agreed within the estimated 25% accuracy of XPD. (Trace amounts of ammonia in the laboratory may have neutralized any acidic sulfate in the samples.) Much of the Al, Si, K and Fe in fine particles was detected as biotite, a clay mineral.

Most Pb in the fine fraction was detected by XPD as lead ammonium sulfate. Later in this report it will be shown that typically 80% of ambient Pb in the Philadelphia area is emitted from vehicles that burn leaded gasoline, which contains PbBrCl. Studies have shown that the Br/Pb ratio for fresh auto exhaust is 0.45 ± 0.06 and is typically much lower for ambient aerosol[30]. Data in Table 2 indicate that the Pb/Br ratio at site 28 is 0.12 ± 0.01. The occurrence of lead ammonium sulfate is a likely consequence of reactions between PbBrCl and ammonium sulfate on the filter. Such reactions volatilize Br and Cl and cause the lower Br/Pb ratios observed for ambient aerosol.

In the coarse fraction, the most abundant species detected by XPD were quartz and clay minerals such as microcline and muscovite, and XRF and XPD measurements for Si generally agree within the 30% accuracy of XPD. Deviations between XRF and XPD are larger for Al, K, and Fe. Such elements are abundant in clay minerals, which are more difficult to measure by XPD. Alkaline minerals such as calcite and dolomite were detected in the coarse fraction, and their presence could account for the nitrate observed in coarse particles. Halite (NaCl) was also detected in coarse particles, and halite can react with HNO_3 vapor to form particulate $NaNO_3$.

TABLE 5. XPD AND XRF RESULTS FOR FINE PARTICLE SAMPLE COLLECTED AT SITE 28 FOR THE 12-HOUR PERIOD BEGINNING AT 0600 ON AUGUST 6, 1982

Analysis Date =26-OCT-84 File = PL120 X-Ray Flux =0.8180
#247914F PHILADELPHIA, PA. 27-JUL-83

Standard	# Lines Found/Poss Major	Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Mascagnite	1 1	15 15	18.76	0.09	0.59	64.137	19.244
2*Teflon	1 1	4 9	24.87	0.34	0.00	0.000	0.000
3*Lead Amm Sulfate	2 2	10 15	2.39	0.09	2.32	2.074	0.627
4*Biotite	1 2	4 10	3.21	0.20	1.60	4.047	1.240
5*MASCAGNITE 2ND-SET	2 2	8 15	1.06	0.05	0.00	0.000	0.000
6*Mascagnite-Prefrd Or	1 1	3 11	1.52	0.16	11.50	0.267	0.085

Total Crystalline Mass = 70.526 ug/cm2

Beta Mass = 95.112 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	3983.			
Li	2.			
N	13787.			
O	33433.			
F	45.			
Na	18.			
Mg	198.			
Al	310.	281.	-29.	110.1
Si	693.	797.	104.	86.9
P	0.	4.	4.	0.0
S	15937.	12505.	-3432.	127.4
K	275.	275.	-0.	100.0
Ca	25.	150.	124.	17.0
Ti	83.	61.	-22.	136.1
V	0.	54.	54.	0.0
Mn	8.	13.	5.	64.0
Fe	739.	545.	-194.	135.7
Ni	0.	17.	17.	0.0
Cu	0.	40.	40.	0.0
Zn	0.	90.	90.	0.0
Se	0.	2.	2.	0.0
Br	0.	70.	70.	0.0
Rb	0.	5.	5.	0.0
Sr	0.	3.	3.	0.0
Cd	0.	2.	2.	0.0
Sn	0.	5.	5.	0.0
Sb	0.	4.	4.	0.0
Pb	987.	717.	-270.	137.6

Sample Attenuation 0.49% from XPD and 0.32% from XRF

TABLE 6. XPD AND XRF RESULTS FOR COARSE PARTICLE SAMPLE COLLECTED AT SITE 28 FOR THE 12-HOUR PERIOD BEGINNING AT 0600 ON AUGUST 6, 1982

Analysis Date =26-OCT-84 File = PL121 X-Ray Flux =0.8180
#147914C PHILADELPHIA, PA. 27-JUL-83

Standard	# Lines Found/Poss Major	Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Teflon	1 1	4 9	54.32	0.44	0.00	0.000	0.000
2*Quartz	1 1	7 8	18.62	0.08	1.98	18.940	5.683
3*Soda Niter - NaNO3	1 1	2 6	4.00	0.06	1.49	5.401	1.622
4*Microcline	2 2	5 10	1.65	0.05	0.62	5.313	1.603
5*Muscovite	1 1	7 15	1.29	0.14	0.40	6.505	2.075
6*Halite NaCl	1 1	2 3	4.50	0.29	3.15	2.878	0.883
7*Dolomite	1 1	2 6	1.71	0.08	1.53	2.253	0.684

Total Crystalline Mass = 41.290 ug/cm2

Beta Mass = 78.966 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	36.			
Li	7.			
C	289.			
N	889.			
O	19902.			
F	16.			
Na	2677.			
Mg	316.			
Al	1622.	2581.	959.	62.8
Si	11871.	9812.	-2059.	121.0
P	0.	83.	83.	0.0
S	0.	658.	658.	0.0
Cl	1746.	928.	-818.	188.1
K	1135.	734.	-401.	154.6
Ca	539.	1031.	491.	52.3
Ti	23.	433.	411.	5.3
V	0.	33.	33.	0.0
Cr	23.			
Mn	5.	21.	16.	25.0
Fe	119.	2477.	2358.	4.8
Ni	0.	8.	8.	0.0
Cu	0.	15.	15.	0.0
Zn	0.	43.	43.	0.0
Br	0.	30.	30.	0.0
Rb	0.	3.	3.	0.0
Sr	0.	8.	8.	0.0
Sb	0.	18.	18.	0.0
Ba	41.	41.	1.	97.6
Pb	0.	118.	118.	0.0

Sample Attenuation 0.30% from XPD and 0.40% from XRF

SECTION 4

RESULTS AND DISCUSSION

COMPOSITE METHOD DESCRIPTION AND RESULTS

The composite method consists of a wind-trajectory method to identify sources, chemical mass balance (CMB) to determine their contributions to PM-10, and CMB combined with multiple linear regression (MLR) to determine a sulfur-component and vehicle exhaust.

Wind-Trajectory Method to Identify Sources to Include in CMB

The wind trajectory method was used to identify cases of high species concentrations when wind vectors were steady in direction and pointed from source to receptor[12]. Hourly data on surface winds at Philadelphia International Airport were used to compute resultant wind direction Θ and standard deviation $\delta\Theta$ for each 12-h period. Mean concentration $\bar{x}$ and standard deviation s were calculated for each species. Events were selected with $\delta\Theta \leq 20^{\circ}$ and $x \geq \bar{x} + 2s$. The wind direction criterion was satisfied for about 18 of the 12-h periods, and both criteria were satisfied for one or two periods, depending on the species. Emission sources along the direction of the wind vector were identified when element abundance ratios matched those of source signatures[10,13]. Table 7 shows aerosol compositions for several periods that met both criteria. Some periods listed in Table 7 represent winds from the southwest where multiple sources may contribute to each sample.

The wind-trajectory method selected two periods on July 21-22 when winds were from the northwest. For one period, fine particle abundances of Na, K, Zn, Cd, Sn and Pb site 28 were at maxima, and their ratios matched within 2σ those measured at an incinerator[10] 15 km northwest of site 28. (Here σ includes uncertainties in source and ambient data.) Another incinerator 4-km northwest of site 28 (Figure 1) could have been the major contributor. Ambient nitrate and Cl also had maxima during the event, but Cl was very deficient and NO_3^- was enriched relative to incinerator emissions. Reactions between atmospheric HNO_3 and NaCl and KCl from incinerators could cause such Cl loss and NO_3^- gain. Similar Cl loss was observed in Washington, DC[31].

The wind-trajectory method selected other events with elevated Ti or Sb concentrations and indicated a paint pigment plant and an Sb roaster, both 6 km southwest of Site 28 (Figure 1). At night on July 18-19, Sb concentrations were very high in both size fractions. Also selected were events with elevated V, Ni and Mo concentrations in ratios within 2σ of emissions from oil-fired power plants. Other events had elevated La, Ce and Sm concentrations with ratios that matched catalytic cracker emissions[10] within a factor of 2. Several such sources were in the area, but specific ones were not identified. Catalytic cracker emissions were detected only in fine particles because INAA, needed to determine La, Ce and Sm, was not applied to ambient coarse particles. Source measurements indicated that the coarse fraction was insignificant[10].

TABLE 7. AEROSOL COMPOSITION AT SITE 28
DURING EVENTS SELECTED BY WIND-TRAJECTORY METHOD[‡]

	Jul 18 1800		Jul 19 1800		Jul 21 1800		Aug 5 0600	Aug 6 1800		Aug 9 1800	
θ =	237°		263°		318°		239°	96°		229°	
$\delta\theta$ =	14°		18°		20°		17°	31°		21°	
	Sb Roast		Oil-Boiler		Incinerator		FCC[#]	Marine[+]		Paint Pig.	
	F	C	F	C	F	C	F	F	C	F	C
NO3	-76	119	12	327	635	318	18	188	1095	-12	434
VC	2533	-91	1081	635	2656	545	4123	861	1182	623	412
NVC	1755	157	2163	817	1176	514	3688	586	171	1532	226
Mass	49596	18170	37817	16700	20458	14736	64309	6802	9202	24422	7477
XRF data											
Al	-65	388	43	616	64	747	110	31	129	42	118
Si	83	1766	135	1856	174	1903	215	70	704	101	315
S	7835	291	6165	364	1224	178	10712	957	150	3879	223
Cl	-40	-42	-16	22	443	244	-12	3	1380	-3	14
K	26	138	39	170	897	260	136	24	102	37	81
Ca	35	253	50	447	82	485	51	20	137	30	78
Ti	44	119	15	77	15	67	58	18	18	98	172
V	3	2	54	26	27	4	23	8	4	28	12
Mn	9	6	13	41	19	16	7	2	1	3	-1
Fe	53	394	147	700	116	513	119	57	241	101	171
Ni	10	4	38	16	6	2	11	3	1	14	6
Zn	6	4	44	41	876	154	28	8	5	13	51
Br	11	10	14	12	77	25	21	41	15	17	10
Cd	-1	5	1	1	13	2	-2	-5	-2	-3	
Sn	-2	-5	2	-1	55	10	8	2	-3	4	-3
Sb	1105	2670	98	289	16	7	4	-3	4	94	126
Pb	146	44	155	39	837	134	196	207	49	155	28
INAA data											
Na	68		83		936		131	+		83	
Al	77		72		57		113	+		58	
Sc*	15		18		35		26	+		15	
V	8		41		4		16	+		28	
Cr	<1		8		2		2	+		2	
Co*	538		1763		486		317	+		464	
As*	<1		296		1499		1288	+		264	
Se*	2702		1921		2027		3557	+		1467	
Mo*	<1		1414		1129		844	+		1045	
Ag*	<1		<1		1341		676	+		<1	
La*	538		2607		359		4592	+		2143	
Ce*	1668		982		<1		1319	+		992	
Sm*	65		50		39		117	+		53	

*Asterisk (*) indicates data in pg/m^3; all other data are in ng/m^3.
+The criterion $\delta\theta \leq 20°$ was not satisfied, and INAA data are not available.
#Fluidized catalytic cracker (FCC).
‡Negative concentrations are below detection limits and have no significance.

Table 7 show an example of one of the samples collected between August 6 and 8 when coarse particle Cl had maxima at all three sites. Surface winds on August 6 in Philadelphia, Wilmington, Atlantic City and Newark were from the east, and this suggests that marine aerosol from the Atlantic Ocean is a likely source of the Cl during this event.

CMB Analysis of Philadelphia Aerosol

The CMB method expresses measured concentration C_i of species i as

$$C_i = \Sigma A_{ij} T_j + \delta_i \qquad (1)$$

where A_{ij} is the abundance of species i in component j, and T_j is the mass concentration of source component j. This equation is solved for T_j by minimizing χ^2 defined as follows in terms of residuals δ, number of species N_s, number of components N_c and effective variance[32] E_i^2:

$$\chi^2 = (N_s - N_c)^{-1} \Sigma (\delta_i / E_i)^2 \qquad (2)$$

Five industrial sources identified by wind-trajectory-analysis and crustal matter met the criteria outlined in the Introduction and were included in the CMB for fine particles. The signatures are shown in Appendix C. The signatures for dust and paint-pigment manufacturing were from refs. 11 and 33, respectively, and the others were from ref. 10. Table 8 shows results of CMB applied to the average composition of fine particles at site 28. The computations were performed by a computer program developed by the author. Note that only 10% of the measured fine mass is explained by this CMB; a composite of CMB and MLR described below explains most of the remainder.

TABLE 8. FINE-PARTICLE CMB FOR AVERAGE AEROSOL COMPOSITION AT SITE 28+

		(Observed)	(Calculated)	Dust	Oil-Av	Paint	CatCr	Incin	Sb
In CMB									
Al	INAA	53 ± 6	43 ± 15	21	5	2	14	2	0
Si	XRF	103 ± 21	127 ± 37	79	16	0	20	12	0
Ti	XRF	15 ± 9	17 ± 9	3	1	12	1	0	0
V	INAA	13 ± 1	11 ± 3	0	11	0	0	0	0
Fe	XRF	91 ± 7	79 ± 26	57	12	9	0	2	0
Ni	XRF	11 ± 2	12 ± 3	0	12	0	0	0	0
Zn	XRF	82 ± 6	82 ± 7	1	7	0	0	74	0
Cd	XRF	2 ± 1	1 ± 1	0	0	0	0	1	0
Sn	XRF	5 ± 4	5 ± 4	0	0	0	0	5	0
Sb	XRF	79 ± 8	79 ± 9	0	0	0	0	1	78
La*	INAA	1120 ± 126	900 ± 201	17	204	0	679	1	0
Ce*	INAA	609 ± 97	757 ± 182	43	158	0	555	0	0
Sm*	INAA	40 ± 5	50 ± 15	6	9	0	35	0	0
Not in CMB									
S	XRF	4196 ± 287	116 ± 287	1	84	0	9	21	1
Pb	XRF	249 ± 15	55 ± 18	3	10	0	0	41	0
Mass	β	28282 ± 3124	2711 ± 3133	936	703	54	206	714	99

+N_c = 6, N_s = 13, χ^2 = 0.71, R^2 = 0.98, and number of iterations = 7.
*Asterisk (*) indicates data in pg/m³; all other data are in ng/m³.

Table 9 shows a CMB based on the average composition of coarse particles at site 28. Signatures used in the CMB for coarse particle included municipal incinerators[10], an Sb ore roaster[10], and average surface soil from the Philadelphia area[11] and are shown in appendix D. Because ammonium was not present in the coarse fraction (Table 2), the 33% abundance of S in sulfate was used for the coarse sulfate component. The marine signature was from ref 13; the Cl abundance was 40%, which is lower than that of dried sea water and represents some loss of Cl. The marine component has large uncertainty because it was determined almost exclusively by Cl, an element that is volatilizable in the presence of nitric acid vapor. Indeed, Table 7 shows high nitrate for the marine event, an indication that HNO_3 has reacted with NaCl particles. The CMB solution for the marine component was constrained to non negative values, which caused the result to be zero. This is discussed further below.

Because vehicle exhaust contributed little to the mass concentration of coarse particles, it could not be determined by the composite of CMB and MLR and had to be determined by CMB. The vehicle exhaust signature shown in Appendix D for coarse particles is based partly on the 7.1 ± 1.6% Pb abundance derived for fine particles using the composite of MLR and CMB described below. Abundances of other elements in vehicle exhaust (S, Cr, Mn, Fe, Ni and Br) were taken from Pennsylvania Turnpike tunnel data[34] adjusted for the vehicle mix in Philadelphia from ref. 16.

TABLE 9. COARSE-PARTICLE CMB FOR AVERAGE AEROSOL COMPOSITION AT SITE 28*,+

	Calculated	Observed	Soil	Marine	Incin	Vehicl	Sb	SO4
In CMB								
Al	478 ± 230	549 ± 169	451	0	22	4	1	0
Si	1796 ± 560	1613 ± 387	1753	0	37	7	0	0
S	230 ± 140	230 ± 139	24	0	14	9	3	181
Cl	70 ± 22	69 ± 13	2	0	60	6	2	0
Ti	81 ± 18	65 ± 12	71	0	7	1	2	0
Fe	447 ± 70	493 ± 37	432	0	7	7	0	0
Zn	24 ± 16	30 ± 4	4	0	18	1	0	0
Cd	0 ± 4	0 ± 2	0	0	0	0	0	0
Sb	180 ± 34	181 ± 13	0	0	0	0	180	0
Pb	54 ± 12	54 ± 5	4	0	7	43	0	0
Not in CMB								
NO3	56 ± 181	573 ± 177	51	0	0	5	0	0
K	125 ± 28	151 ± 23	104	0	19	2	0	0
Ca	165 ± 51	363 ± 37	115	0	43	7	0	0
V	1 ± 4	7 ± 4	1	0	0	0	0	0
Mn	6 ± 3	11 ± 3	5	0	0	1	0	0
Ni	3 ± 1	4 ± 1	3	0	0	0	0	0
Br	14 ± 7	15 ± 1	0	0	1	13	0	0
Sn	0 ± 5	1 ± 3	0	0	0	0	0	0
Mass	8534 ± 2813	11433 ± 2793	6721	0	427	599	240	548
Unc.	±964	±2793	±821	±148	±148	±169	±45	±426

+N_c = 6, N_s = 10, χ^2 = 0.42, R^2 = 0.99, and number of iterations = 5.
*Data are in ng/m³.

Average Mass Concentrations Deduced by CMB

Apportionments shown in Tables 8 and 9 were obtained by applying CMB to the average aerosol composition. An alternative is to apply CMB to each sample and then compute an average for each component. CMB computations were made for each sampling period using the same fitting elements and signatures as in Tables 8 and 9, and results for site 28 are illustrated in Appendices E and F. Table 10 shows the average component concentrations and average uncertainties for each site. CMB results in Table 10 agree with those in Tables 8 and 9 within the stated uncertainties. The sulfur-component and vehicle exhaust were determined not by CMB but by a method described below.

Some of the CMB results in Appendices E and F are small negative values, which are a normal consequence of species concentrations below detection limits. Except for the marine component, negative values were included in the averages because biased solutions occur if they are deleted. However, the marine component was constrained to non negative values in order to reduce a larger bias that occurred because Cl, a volatilizable element, was included in the CMBs. When Cl volatilizes from incinerator particles, an unconstrained CMB assigns a negative marine component to the difference between Cl abundances in incinerator particles at source and receptor. Such problems would not occur if Na data were used to determine the marine component, but INAA data for Na were not available for coarse particles in this study.

TABLE 10. RESULTS OF COMPOSITE RECEPTOR METHOD*

Component	Method	Site 12	Site 28	Site 34
Fine				
Sulfur-component	CMB-MLR	19.1 ± 0.9	20.9 ± 0.8	17.7 ± 1.0
Vehicle exhaust	CMB-MLR	1.6 ± 0.9	3.8 ± 0.9	3.0 ± 1.2
Regression intercept	CMB-MLR	3.9 ± 1.4	1.4 ± 1.2	3.8 ± 1.7
Crustal matter	CMB	1.1 ± 0.3	1.0 ± 0.3	0.7 ± 0.2
Oil-fly ash	CMB	0.5 ± 0.1	0.7 ± 0.1	0.4 ± 0.1
Paint pigment	CMB	0.02 ± 0.04	0.05 ± 0.04	0.01 ± 0.04
Catalytic cracker	CMB	0.13 ± 0.03	0.18 ± 0.05	0.09 ± 0.03
Incinerator	CMB	0.6 ± 0.1	0.7 ± 0.1	0.20 ± 0.03
Sb-roast	CMB	0.01 ± 0.01	0.09 ± 0.01	0.00 ± 0.01
Coarse				
Crustal matter	CMB	4.6 ± 0.6	6.7 ± 0.8	3.5 ± 0.4
Sea salt	CMB	0.13 ± 0.16	0.2 ± 0.2	0.09 ± 0.10
Sulfate	CMB	0.4 ± 0.4	0.6 ± 0.4	0.7 ± 0.4
Incinerator	CMB	0.18 ± 0.15	0.07 ± 0.20	0.06 ± 0.09
Vehicle exhaust	CMB	0.5 ± 0.2	0.7 ± 0.2	0.3 ± 0.1
Sb-roast	CMB	0.02 ± 0.01	0.23 ± 0.05	0.01 ± 0.01
Coal-fly ash	SEM-EDX	0.10 ± 0.05	0.20 ± 0.09	
Botanical matter	SEM-EDX	2.0 ± 0.9	1.7 ± 0.8	
PM-10				
Calculated total		34.9 ± 2.3	39.0 ± 2.1	30.6 ± 2.4
Measured total	β-gauge	34.9 ± 4.2	39.7 ± 4.2	33.9 ± 4.1

*Results are in $\mu g/m^3$. Calculated totals do not include SEM data for coal-fly ash because coal-fly ash is included in crustal matter determined by CMB.

Composite of CMB and MLR

If unique tracers are available, MLR is an effective receptor method that can be used even if source signatures are unknown[35,36]. Lead is a tracer for vehicles that burn leaded gasoline and can serve as a tracer for the entire fleet of vehicles if traffic patterns are similar. However, Table 8 shows that Pb is not a unique tracer for vehicle exhaust because non vehicular sources contribute 22% of average ambient Pb at site 28. In one sample municipal incinerators contributed 61% of ambient Pb. This problem is overcome by a composite method that uses CMB results to derive unique tracers M′, S′, and Pb′, which represent concentrations of mass, S and Pb due only to the sulfur-component and vehicle exhaust:

$$M' = M - \Sigma T_j \quad (3a)$$

$$S' = S - \Sigma A_{S,j} T_j \quad (3b)$$

$$Pb' = Pb - \Sigma A_{Pb,j} T_j \quad (3c)$$

Here M, S and Pb are the measured concentrations of mass, S and Pb. Data for each 12-hour sampling period were analyzed by CMB in the manner shown in Table 8, and the resulting data were used in equation 3 to compute M′, S′ and Pb′, which were used in the following MLR:

$$M' = a + bS' + cPb' + \varepsilon \quad (4)$$

Coefficients a, b and c were determined by a least-squares procedure[37] that minimized the sum of squares of residuals ε. Appendix G shows a printout of MLR results obtained by applying equation 4 to data for site 28. Table 11 shows results for MLR applied to all data and to data for each site.

TABLE 11. MULTIPLE LINEAR REGRESSION RESULTS BY SITE

N	constraint	Regression results[a]	R^2
156	none	M′ = 3.6 ± 0.8 + (4.9 ± 0.1)S′ + (14 ± 3)Pb′	0.90
52	site 12	M′ = 3.9 ± 1.4 + (5.0 ± 0.2)S′ + (9 ± 5)Pb′	0.91
50	site 28	M′ = 1.4 ± 1.2 + (5.1 ± 0.2)S′ + (19 ± 4)Pb′	0.94
54	site 34	M′ = 3.8 ± 1.7 + (4.6 ± 0.3)S′ + (26 ±10)Pb′	0.87

[a]Intercept has units of μg/m³.

Average Component Concentrations Deduced by Composite of MLR and CMB

According to equation 4, a component's average concentration is the product of its regression coefficient and its mean tracer species concentration. Averages obtained in this manner are shown for each site in Table 10. The following is an illustration of this computation for site 28 based on the MLR results in Appendix G:

S-comp. = [mean S′] x [b] = [4.08 μg/m³] x [5.12 ± 0.19] = 20.9 ± 0.8 μg/m³
Veh. exh. = [mean Pb′] x [c] = [0.195 μg/m³] x [19.3 ± 4.4] = 3.8 ± 0.9 μg/m³

Scanning Electron Microscopy

Coarse particles were analyzed for morphology by SEM and for composition by energy dispersive x-ray spectrometry (EDX). Both morphology and x-ray spectra were needed to distinguish among particles[15]. Masses were estimated from observed dimensions and assumed densities[15], and examples of results are shown in Table 12. Accuracy estimates were based on 15% uncertainty in density, 40% uncertainty in estimating particle volume, and counting statistics.

TABLE 12. SCANNING ELECTRON MICROSCOPY RESULTS FOR COARSE PARTICLES AT SITE 28

Category	Diameter Range* ≤1.5	≤2.1	≤3.1	≤5.1	≤7.1	≤10	Mass, μg m^{-3} SEM	CMB
Day								
Mineral, soil	1	15	26	29	10	6	7.7 ± 3.1	3.7 ± 1.2
Cl-rich mineral			1				0.01 ± 0.05	na
Incinerator	1		3	1			0.1 ± 0.1	1.0 ± 0.6
Coal-fly ash		1		1			0.06 ± 0.06	na
Botanical		11	23	33	6	2	2.3 ± 0.9	na
Night								
Mineral, soil	1	36	38	30	8	1	8.5 ± 3.4	5.8 ± 2.1
Cl-rich mineral		2	2	6	1	1	2.1 ± 0.8	
Incinerator	3	13	10	10	1		1.8 ± 0.7	3.2 ± 1.3
Zn-rich			1		1		0.41 ± 0.2	na
Coal-fly ash	6	17	7	4			0.7 ± 0.3	na
Botanical		4	11	9	4	1	2.0 ± 0.8	na

*Coarse particle count and estimated mass concentration by category at Camden, NJ, for 12-h periods beginning at 0600 and 1800 on July 21, 1982.

Table 10 shows average mass concentrations of coal-fly ash and botanical particles based on SEM analysis of five samples at site 12 and seven samples at site 28. SEM results were obtained for other categories, which were also determined by CMB and are not shown in Table 10. CMB results for "soil" shown in Table 10 include coal-fly ash because their signatures were collinear. Thus, SEM results for coal-fly ash were not included in the "calculated totals" shown in Table 10. Furthermore, the few samples analyzed by SEM were not chosen randomly, and this causes the SEM-based averages not to represent the mean for the 50-54 sampling periods represented by Table 10.

Origin of Sulfur-Component

According to Table 10, the sulfur-component accounts for 54 ± 10% of PM-10 mass concentration. An earlier report used time series plots and data at upwind and downwind sites to estimate that 80 ± 20% of particulate S in the Philadelphia area originated from sources beyond that area[8]. MLR analyses of S vs V and Se attributed 72 ± 8 of fine particle S to coal burning and 16 ± 5% to oil burning[8].

EVALUATION OF COMPOSITE RECEPTOR METHOD

The above section described apportionments based on the composite receptor method. This section provides an evaluation of their accuracy and attempts to answer questions about their sensitivity to choices of signature, measurement method and data subset.

Accuracy of CMB Code

CMB computations described above were made by a FORTRAN code developed by the author. It was optimized to provide results in a format needed for the composite of CMB and MLR. To test the accuracy of the author's CMB code additional computations were made by an EPA code developed by contractors[5]. Appendix H shows a printout of the EPA code applied to the average composition at site 28. Results in Appendix H can be directly compared to results shown in Table 8 because the same ambient data and source signatures were used. Both sets of results agree within 0.4%. The calculated uncertainties differ only because they were defined differently. Those in Table 8 include uncertainties in both measured concentrations and source signatures whereas calculated uncertainties shown in Appendix H only include the latter.

A unique feature of the EPA code is that it identifies source signatures that may be collinear[5,38]. Appendix H identifies paint-pigment and catalytic-cracker components as belonging to an "uncertainty/similarity cluster". In general, such pairing indicates that either (1) one or both components have large uncertainty or (2) their signatures are collinear[5]. In this instance the former applies because the paint pigment component has a large standard error and a t-statistic smaller than 2. Collinearity was not the problem.

Sensitivity of CMB Results to Choice of Source Signatures

To determine the sensitivity of CMB results to choice of signatures, the average composition at site 28 was analyzed by CMB using a variety of signatures. Table 13 and 14 present the results and identify the signatures. The signatures are tabulated in Appendices C and D.

Fine particle results for crustal matter, shown in Table 13, are very sensitive to the signature for crustal matter. Locally obtained signatures for dust and soil yielded the lowest values of χ^2, which indicates that they best represent the elemental ratios for crustal matter. However, the mass normalization for the local signatures is poor because the fine particle samples used in the analysis were so lightly loaded that the measured mass was close to the detection limit and highly uncertain. Thus, mass normalizations for Al and Si in the soil and dust signatures are about a factor of 3 lower than those of the Medford, OR[13] and earth's crust[39]. This explains the wide divergence among results for crustal matter. Fortunately, fine fraction crustal matter concentrations are so low that their factor of 3 normalization error causes only a 10% error in total crustal concentration in the PM-10 size range.

The paint pigment component is highly sensitive to choice of signature used for the crustal component. The "uncertainty/similarity cluster" index noted above also indicated that the paint pigment component was too small to be determined reliably.

TABLE 13A. DEPENDENCE OF FINE FRACTION CMB ON SOURCE SIGNATURES*

Signatures used	Component concentration in ng/m³						
	Crustal matter	Oil	Paint pig.	Cat. cracker	Munic. incin.	Sb roast.	χ^2
1 6 8 10 11 13	936	703	54	206	714	99	0.7
1 4 8 10 11 13	942	593	54	189	739	99	0.8
1 5 8 10 11 13	889	956	56	233	666	100	0.8
1 6 8 10 14 13	1058	706	43	205	628	99	0.7
2 4 8 10 11 13	546	608	87	174	742	99	1.7
2 6 8 10 11 13	539	741	87	188	714	99	1.5
9 6 8 10 11 13	331	861	176	181	700	99	4.5
15 6 8 10 11 13	408	826	162	178	704	99	3.9
15 6 8 10 14 13	592	793	116	175	625	99	3.3

*CMB was applied to the average fine particle composition at site 28. Fitting elements were Si, Ti, Fe, Ni, Zn, Cd, Sn and Sb measured by XRF and Al, V, La, Ce and Sm. However, Si was not used as a fitting element when signature 14 was used because Si data were not available for signature 14.

TABLE 13B. IDENTIFICATION OF SIGNATURES USED IN TABLE 13A

Signature number	Signature name	Description	Measured size range	Measurement Location	Ref.
1	Dust	Resuspended street dust	fine	Philadelphia-Camden area	11
2	Soil	Resuspended soil 2-20 mm deep	fine	Same as above	11
4	Oil-Sk	Schuylkill oil-fired boiler	fine	Philadelphia	10
5	Oil-Ed	Eddystone oil-fired boiler	fine	Philadelphia	10
6	Oil-Av	Average of signatures 4 & 5	fine	Philadelphia	
8	Paint	Paint pigment in ambient air	fine	St. Louis, MO	33
9	SoilMed	Soil dust (Profile 41318)	fine	Medford, OR	13
10	CatCr	Fluidized catalytic cracker	fine	Camden area	10
11	Incin	Municipal Incinerator	fine	Philadelphia	10
13	Sb	Antimony Roaster	fine	Camden area	10
14	IncComp	Munic. incin. (Profile 11706)	total	Composite	13
15	Earth	Earth's crust	n. a.	Global	39

TABLE 14A. DEPENDENCE OF COARSE FRACTION CMB ON SOURCE SIGNATURES*

Signatures used	Component concentration in ng/m^3						
	Crustal matter	Marine	Munic. incin.	Vehicle	Sb roast.	Sulfate	χ^2
2 8 11 12 13 16	6716	0+	424	640	240	546	0.4
2 8 15 12 13 16	6959	32	210	485	240	561	0.3
2 8 11 12 13 16	6696	-14	456	633	240	545	0.4
1 8 11 12 13 16	7061	0+	475	-57	242	597	1.8
1 8 11 12 13 16	6835	0+	470	0+	242	596	1.8
1 8 11 12 13 16	6175	-265	1230	-156	241	561	1.7
4 8 11 12 13 16	8205	0+	455	693	243	599	1.1
9 8 11 12 13 16	7139	-60	600	663	241	590	0.7
9 8 11 12 13 16	7208	0+	450	700	241	597	0.8

*CMB was applied to the average coarse particle composition at site 28. Fitting elements were Al, Si, S, Cl, Ti, Fe, Zn, Cd, Sb and Sb measured by XRF. However, Si was not used as a fitting element when signature 15 was used because Si data were not available for signature 15.

+CMB solutions were constrained to non negative values.

TABLE 14B. IDENTIFICATION OF SIGNATURES USED IN TABLE 14A

Signature number	Signature name	Description	Measured size range	Measurement Location	Ref.
1	Dust	Resuspended street dust	coarse	Philadelphia-Camden area	11
2	Soil	Resuspended soil 2-20 mm deep	coarse	Same as above	11
4	Earth	Earth's crust	n. a.	Global	39
8	Marine	Marine Aerosol (Profile 43101)	coarse	Philadelphia	13
9	SoilMed	Soil dust (Profile 41318)*	coarse	Medford, OR	13
11	Incin	Municipal Incinerator	coarse	Philadelphia	10
12	Vehicl	Vehicle emissions, see text			
13	Sb	Antimony Roaster	coarse	Camden area	10
15	IncComp	Munic. incin. (Profile 17106)	total	Composite	13
16	Sulfate	Sulfate only	n. a.	n. a.	

*Abundance of Si in profile was multiplied by 10 to correct for an apparent error in the published data.

Signatures were measured for two different oil fired power plants in Philadelphia[10]. Use of either signature rather than their average causes the fine particle oil component to change by about 30%. Use of a composite profile for municipal incinerators[13] rather than the locally measured one[10] changes the fine particle results by less than 15%.

In contrast to fine particles, the crustal component for coarse particles is much larger and much less sensitive to source signature. This occurs because the normalization for Al and Si is much more similar for the various signatures. However, the vehicle exhaust component is very sensitive to choice of crustal signature. If the dust signature is used, the vehicle component is close to zero because there is enough Pb associated with the dust signature to explain all the Pb in atmospheric coarse particles. However, because the other crustal signatures have low Pb abundances, their use causes atmospheric Pb to be attributed to vehicle exhaust. Thus, the amount of coarse particle vehicle exhaust at site 28 is ambiguous over the range 0 to 0.7 $\mu g/m^3$. Although there is little doubt that most of the atmospheric coarse particle Pb came from vehicle exhaust, it is uncertain whether it came from direct emissions or from Pb in the roadway that was resuspended by vehicles. Since fine particle vehicle exhaust at site 28 is 3.8 ± 0.8 $\mu g/m^3$, the coarse particle ambiguity amounts to less than 20% of total vehicle exhaust in the PM-10 range.

Table 14 shows that the municipal incinerator component is sensitive to whether or not a constraint of non negativity is applied to the marine component. As explained above, there were serious problems in determining both the marine and incinerator components. The former was determined by Cl, which is volatile, and the latter was determined mainly by Zn, which may have had sources not included in the CMB.

Sensitivity of CMB Results to Choice of Measurement Method

Table 15 shows apportionments based on the following combinations of measurement data: both XRF and INAA, only XRF and only INAA. When only XRF data were used, fluidized catalytic cracker emissions were not determined because essential elements (La, Se and Sm) were not detected. Except for that component and a marginally detected component from a paint pigment factory, the results are fairly insensitive to choice of measurement method.

Average uncertainties shown in Table 15 are smaller for XRF results than for INAA results. This occurs because more XRF-measured elements were used in the CMBs. Fewer elements were used in the INAA-based CMBs because INAA data were not available for soil signatures in Philadelphia. This eliminated many elements such as Na, Sc, Cr and Co, which are accurately measured by INAA.

A comparison of measurement capabilities indicated that INAA is superior for Na, Al, Se, V, Cr, Mn, Co, As, Se, Rb, Mo, Sb, I, Cs, La, Ce and Sm whereas XRF is superior for Si, S, Ca, Ni, Sr, Sn, and Pb[9]. Both methods are comparable for K, Fe, Zn, and Br[9]. The present study generally confirms those rankings except that Mn and Sb concentrations were high enough to be accurately measured by XRF. Such conclusions about INAA pertain to the National Bureau of Standards' reactor and do not necessarily apply to reactors with lower neutron flux or different energy distribution.

TABLE 15. EFFECT OF MEASUREMENT METHOD ON FINE FRACTION CMB AT SITE 28*

Component	XRF-INAA#	XRF+	INAA@	standard deviation
Crustal matter	1.0 ± 0.3	1.0 ± 0.3	1.4 ± 0.6	0.5
Oil-fly ash	0.7 ± 0.12	0.7 ± 0.14	0.8 ± 0.28	0.5
Paint pigment	0.05 ± 0.04	0.05 ± 0.04	na	0.08
Catalytic cracker	0.18 ± 0.05	na	0.17 ± 0.05	0.2
Incinerator	0.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	1.5
Sb-roast	0.09 ± 0.01	0.09 ± 0.01	0.10 ± 0.01	0.2

*Results are averages in $\mu g/m^3$ for the period July 14 to August 13, 1982.

#Based on XRF data for Si, Ca, Ti, Fe, Ni, Zn, Cd, Sn and Sb and INAA data for Al, V, La, Ce and Sm.

+Based on XRF data for Al, Si, Ca, Ti, V, Fe, Ni, Zn, Cd, Sn and Sb.

@Based on INAA data for Al, Ca, V, Fe, Zn, Cd, Sb, La, Ce, and Sm.

Sulfate measured by IC was not essential for apportionment of PM-10 and only served to confirm the accuracy of XRF data for S. Nitrate data were of little value because of likely volatilization during sampling. Data on volatilizable carbon in this study had poor precision because sample blanks were large and variable.

A comparison like the one in Table 15 cannot be made for the coarse fraction because INAA was not applied to the coarse fraction.

Evaluation of MLR Results

To determine the sensitivity of MLR results to measurement method or to any anomalous data, equation 4 was applied to all samples and to various sample subsets, and results are shown in Table 16. To assess the consequences of any large CMB error for the incinerator component, results are shown for **Pb/Zn** < 0.27. Such a constraint limits Pb from incinerators to <15% of ambient Pb and eliminates 46 out of 156 observations. Computations were also made for single sites. In other computations only every third or every fifth datum was used; results in Table 16 represent averages for various ways that every third or fifth datum can be selected. Except for the Pb regression coefficient for site 34, which will be discussed later, results in Table 16 are not significantly affected by constraints on Zn, site or sample size.

TABLE 16. MULTIPLE LINEAR REGRESSION RESULTS FOR VARIOUS DATA SUBSETS

N	constraint	Regression results*	R^2
XRF			
156	none	$M' = 3.6\pm0.8 + (14 \pm 3)Pb' + (4.9\pm0.1)S'$	0.90
110	Zn/Pb < 0.27	$M' = 2.4\pm1.0 + (14 \pm 3)Pb' + (5.1\pm0.1)S'$	0.92
52	site 12	$M' = 3.9\pm1.4 + (9 \pm 5)Pb' + (5.0\pm0.2)S'$	0.91
50	site 28	$M' = 1.4\pm1.2 + (19 \pm 4)Pb' + (5.1\pm0.2)S'$	0.94
54	site 34	$M' = 3.8\pm1.7 + (26 \pm 10)Pb' + (4.6\pm0.3)S'$	0.87
52	every 3rd obs	$M' = 3.3\pm1.4 + (16 \pm 6)Pb' + (4.9\pm0.2)S'$	0.90
31	every 5th obs	$M' = 3.2\pm1.8 + (15 \pm 8)Pb' + (5.0\pm0.3)S'$	0.91
156	none	$M' = 3.8\pm0.8 + (71 \pm 20)Br + (5.0\pm0.1)S'$	0.90
148	Zn/Br < 6.8	$M' = 4.1\pm0.8 + (74 \pm 21)Br + (5.0\pm0.1)S'$	0.90
XRF, IC#			
99	sites 12 & 28	$M' = 4.3\pm1.1 + (15 \pm 4)Pb' + (4.8\pm0.2)SO_4^=$	0.89
INAA			
155	none	$M' = 7.4\pm1.3 + (105 \pm 43)Br + (4.6\pm0.2)S'$	0.71
140	Zn/Br < 6.8	$M' = 7.4\pm1.4 + (123 \pm 44)Br + (4.5\pm0.2)S'$	0.71

*Intercept has units of $\mu g/m^3$.
#$SO_4^=$ is expressed as S, 3 outliers are deleted and no data exist for site 34.

Use of Br as a Tracer for Vehicle Exhaust

An advantage of Br as a tracer for vehicle exhaust is that Br has few other significant sources. A disadvantage is that Br volatilizes upon contact with acidic particles, and this makes it difficult to use CMB to estimate the amount of ambient Br due only to vehicles. Thus, a constraint on the **Br/Zn** ratio was used to eliminate cases of significant Br from incinerators, and **Br**, the measured bromine concentration, was used in the following:

$$M' = a + bS' + dBr + \varepsilon \qquad (5)$$

Results are shown in Table 16 both for all observations and for those with **Br/Zn** < 6.8. Such a constraint limits Br from incinerator emissions to less than 15% of ambient Br. The constraint eliminates 8 out of 156 observations and has no significant effect on the results.

Table 17 shows average vehicle exhaust concentrations derived by MLR using all data from all sites. Results based on Br and Pb tracers for vehicle exhaust agree within estimated uncertainties, which are based on standard errors of the regression coefficients. The Br results have the largest percent uncertainties, which may be due to the fact that Br can volatilize upon contact with acid sulfate particles. Thus, the most reliable regression results were based on Pb data.

TABLE 17. EFFECT OF CHOICE OF MEASUREMENT METHOD AND SPECIES ON MLR RESULTS*

Measurement Method for S and Pb	N	Variables	Average concentration, $\mu g/m^3$	
			S-component	Vehicle exhaust
XRF	156	M′ vs S′ and Pb′	19.2 ± 0.5	2.3 ± 0.5
XRF	156	M′ vs S′ and Br	19.6 ± 0.5	1.6 ± 0.4
INAA	155	M′ vs S′ and Br	15.4 ± 0.8	1.8 ± 0.7

Abundances of S and Pb Derived from Regression Coefficients and Model

For coefficients in equation 4, b^{-1} can be interpreted as the S abundance in the sulfur-component and c^{-1} as the Pb abundance in vehicle exhaust. Intercept, **a**, represents additional sources uncorrelated with S and Pb. Abundances derived in this manner from the first row of results in Table 16 are 20.4 ± 0.4% for S in the sulfur-component and 7.1 ± 1.5% for Pb in vehicle exhaust.

Sulfur Abundance in Sulfur-Component--

Sulfate in fine particles at site 28 was reported to be a mixture of ammonium sulfate and ammonium bisulfate[8]. The sulfur-abundance is 24.2% in the former and 27.8% in the latter. Such values are 19% to 36% higher than the S abundance derived from the regression coefficient. The discrepancy has two possible causes: (1) bias in measurement of mass or S and (2) water or carbon in the sulfur-component.

A postulate of $\geq$19% measurement bias is not supported by results of method intercomparisons. For sites 12 and 28, mean IC results for sulfate (expressed as S) and mean XRF results for S agreed within 8%, and the correlation coefficient was 0.98 (Table 4). Furthermore, when sulfate (expressed as an equivalent amount of S) is used as a dependent variable in equation 4, the S abundance derived from the regression coefficient (See Table 16) is 21 ± 1%, which is essentially the same as the result obtained by using S as an independent variable. In a comparison of β-gauge and gravimetric mass measurements in North Carolina, the ratio of means for 136 fine-fraction samples was 1.03, and the slope of a linear relationship was 1.03 ± 0.03[23].

Laboratory studies have demonstrated that ammonium sulfate and ammonium bisulfate aerosol particles can exist in hydrated states at relative humidity below the 55% RH of our mass measurements[40]. However, it is not known if such hydrated states can exist for particles on a filter. Also, the sulfur-

component could include organic carbon, but carbon measurements reported here lack the precision needed to test this possibility.

Pb Abundance in Vehicle Exhaust--

A model for calculating emission factors for Pb and particulate mass from a mixed population of vehicles has been developed by Energy and Environmental Analysis, Inc[41]. The model uses comprehensive data on vehicle emissions as a function of vehicle type and year of manufacture, and a computer code that operates on an IBM-PC is available from EPA's Office of Mobile Sources[42]. It was used in the present study to calculate rates of emission of Pb and mass from engine exhaust for six classes of vehicles. Typical results are shown in Appendix I. Appendix I also shows how abundances of Pb were calculated for emissions from a fleet of vehicles weighted by vehicle-miles traveled (VMT). Emissions include engine exhaust, brake wear and tire wear in particles smaller than 2.5 μm. Cases of urban (Table I1) and Turnpike (Table I2) VMT distributions are shown. VMT distributions in Tables I1 and I2 are based on data for Philadelphia county[16] and Pennsylvania Turnpike[34], respectively. These data were adjusted to correspond to the six vehicle categories used by the model. Table 18 shows Pb abundances for urban and turnpike VMT distributions calculated for various speeds and driving conditions. Effects of presence and absence of governmental programs for inspection and maintenance (IM) of emission control systems are shown. Results are also shown for variable speed driving (trans.) and steady speed driving (cruise). Table 18 shows a tendency for the Pb abundance to decrease as speed increases. Also, it is lower for steady speeds than for transient speeds. Lack of an IM program is predicted to increase Pb abundances by 5%.

TABLE 18. LEAD ABUNDANCE IN 1982 VEHICLE EMISSIONS PREDICTED BY MODEL

Speed		Percent Lead abundance FOR VMT-Weighted Emissions							
		Urban VMT distribution*				Turnpike VMT distribution#			
		With IM		No IM		With IM		No IM	
Speed km/hr	mi/hr	Trans.	Cruise	Trans.	Cruise	Trans.	Cruise	Trans.	Cruise
16	10	10.5	9.1	11.1	9.3	4.8	3.9	5.1	4.1
32	20	8.1	6.3	8.6	6.6	3.5	2.6	3.7	2.7
56	35	6.8	5.8	7.1	6.0	2.8	2.3	3.0	2.5
89	55	6.5	6.2	6.9	6.5	2.7	2.6	2.9	2.7

*VMT is based partly on data for Philadelphia County[16] and is shown in Table I1 of Appendix I.

#VMT is based partly on data for Pennsylvania Turnpike[34] and is shown in Table I2 of Appendix I.

Lead abundances derived by the composite of MLR and CMB are summarized in Table 19. As explained above, the Pb abundance is the reciprocal of the Pb regression coefficient. Three factors affect the Pb abundance derived in this manner: (1) VMT near the sampling site, (2) statistical precision, which is approximately proportional to $\sqrt{N}$, and (3) magnitude of vehicle component. The best precision is obtained for N = 156 when all observations are used. For a cases of a single site, best precision occurs for site 28 where the vehicle component is largest.

TABLE 19. LEAD ABUNDANCE DERIVED FROM REGRESSION COEFFICIENT FOR Pb

Site	Location	Nature of site	Number of obs. N	Mass conc. µg/m3	Regression coefficient for Pb	Percent Pb abundance
all			156	2.3 ± 0.5	14.2 ± 3.2	7.1 ± 1.6
12	Philadelphia, PA	urban	52	1.6 ± 0.9	9.2 ± 5.4	10.9 ± 6.4
28	Camden, NJ	urban	50	3.8 ± 0.9	19.3 ± 4.4	5.2 ± 1.2
34	Clarksboro, NJ	turnpike	54	3.0 ± 1.2	26.4 ±10.4	3.8 ± 1.5

The Pb abundances derived for sites 12 and 28 agree with the value 7.1 ± 1.6% based on data for all sites. However, the Pb abundance derived for site 34 is significantly different from that at other sites but is similar to model predictions for turnpike driving. Thus, the major source of vehicle exhaust at site 34 is probably the New Jersey Turnpike located 1 km to the southeast.

Total Pb emission rates and percent Pb in emissions weighted by VMT in Philadelphia county are plotted vs year in Figures 2 and 3. Figure 3 also shows results derived by MLR from ambient air measurements, which include the present one based on all sites (N=156) and results of other studies[36,43,44]. There is good agreement between the emissions model results and MLR results. Such agreement is encouraging, but sensitivity to input data makes results of the model uncertain. For example, the model assumes that 75% of Pb in fuel is emitted by vehicles, but measurements in a highway tunnel indicate only 50% is emitted[45]. The model allows mass emission rates to vary with speed for light duty vehicles but assumes that emission rates are independent of speed for heavy duty trucks. Also, emissions from motorcycles are assumed to be 100% Pb. Furthermore, the model only considers particles at the tail pipe. When emissions dilute and cool in the atmosphere, volatile organic emissions can condense onto particles and cause the Pb abundance to decrease. Thus, the model results may be uncertain by 30% or more.

(The original version of the computer program for vehicle emissions[42] used incorrect data for the Pb content of gasoline for years beyond 1984. Pb data in reference 41 were used for all computations reported here.)

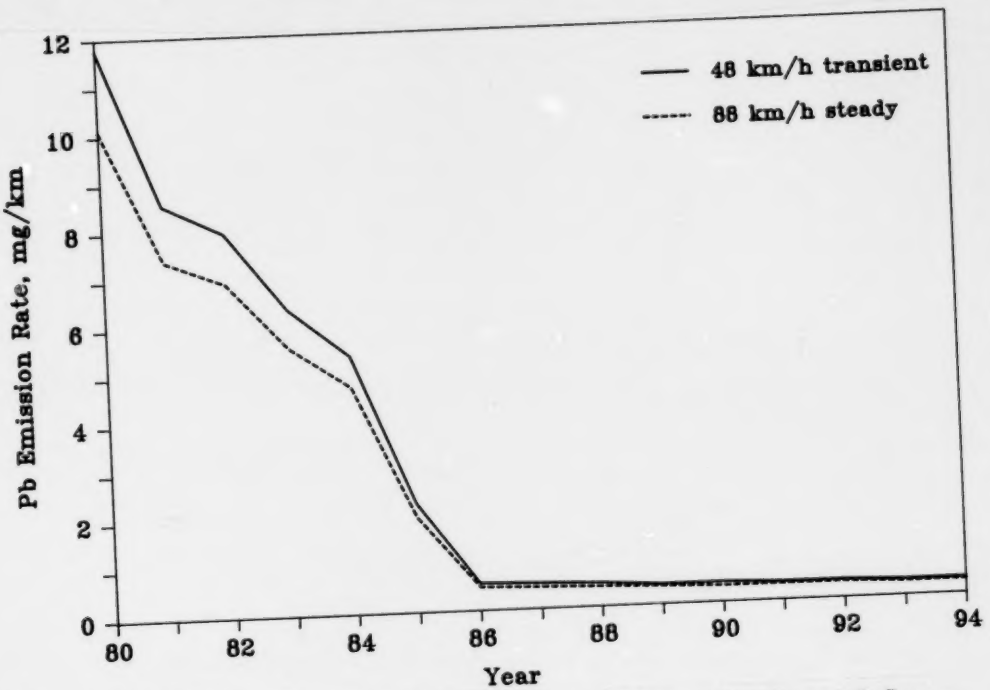

Figure 2. Model results for VMT-weighted Pb emission rate for < 2.5-μm particles from vehicles. (Model results for "LEAD" included Pb, Br and Cl and were divided by 1.557 to obtain emission rates for Pb.)

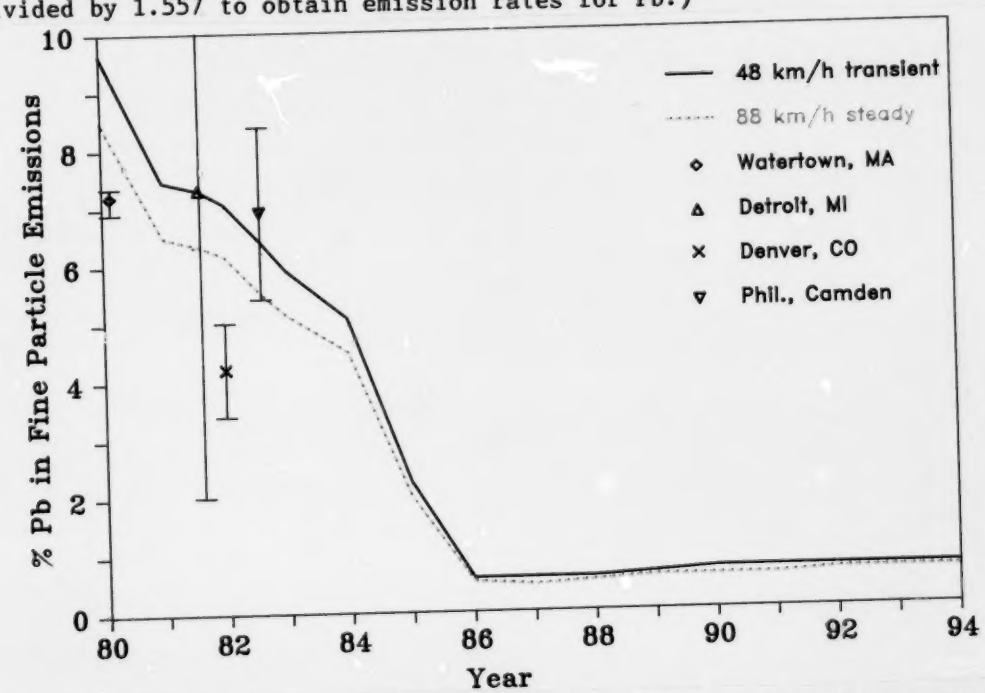

Figure 3. Model results for Pb abundance in < 2.5-μm particle exhaust from a population of vehicles representative of Philadelphia county. Data points represent MLR results for ambient aerosol data as explained in the text.

Evaluation of Scanning Electron Microscopy Results--

Table 12 compares CMB and SEM results for two sampling periods. The period that began at 1800 on July 21 is included in Table 12. Then the incinerator component had its largest value during the study. For that period, site 28 was directly downwind of two large municipal incinerators (See Figure 1 and Table 7), and the CMB and SEM results generally agree within estimated accuracies. Minerals rich in Cl were detected by SEM. Although it is likely that the Cl-rich minerals are associated with incinerator emissions, it is not known if they were emitted by incinerators or if they were the product of reactions between gas phase chlorine from incinerators and minerals from other sources.

Table 12 shows another case where SEM indicated a negligible incinerator component, but CMB detected a large one. The wind direction was 13 ± 22°, and Figure 1 shows no upwind incinerator. The discrepancy could be due either to negative bias for SEM-EDX or positive bias for CMB. Negative bias would occur for the former if Cl, an essential element in SEM determinations, were volatilized from incinerator particles from sources beyond the region shown in Figure 1. Positive bias for CMB results can be explained as follows: Abundant elements in the incinerator component that were included in the CMB were Zn and Cd, but Cd was below its detection limit, which means that the CMB results were actually determined only by Zn. Because incinerators were the only significant sources of Zn in the CMB analyses presented here, Zn from other sources would cause positive bias for CMB based incinerator emissions. Thus, the incinerator component results reported here represent an upper limit.

The standard dichotomous sampler collected fine particles as multiple layers that were unsuitable for analysis by SEM. The multiple layers were mostly sulfate, which coalesced due to deliquescence during high humidity, dried as large sulfate particles, and engulfed non sulfate fine particles[46]. Figure 4 shows a modified dichotomous sampler that collects fine particles on two separate filters. One collects at a low flow rate to avoid pileup. Such a sampler collects both fine and coarse particles in a manner compatible with requirements for analysis by SEM, XRF and INAA[46].

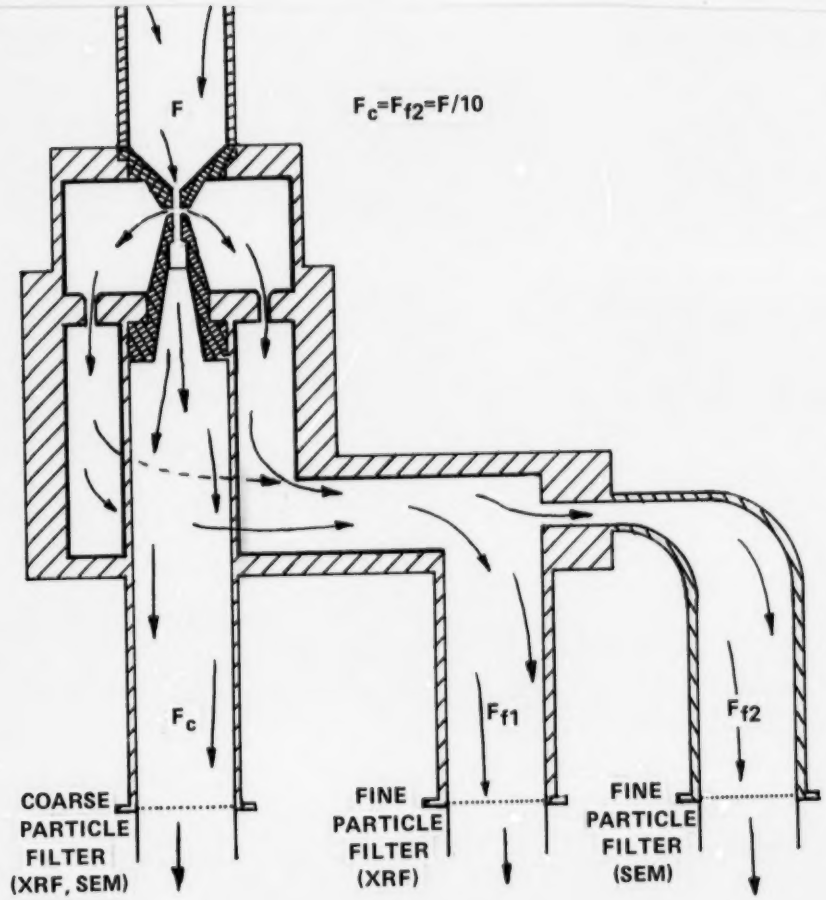

Figure 4. Modified dichotomous sampler that enables samples to be collected for analysis of individual particles and bulk composition.

COST-EFFECTIVE STRATEGY FOR SAMPLING AND ANALYSIS

Evaluation of data for 156 samples suggests a more economical and effective design for PM-10 apportionment than was actually used in the Philadelphia study. Because INAA and SEM-EDX data were not directly used in MLR, it was only necessary to analyze enough samples to provide adequate estimates of the means. Standard errors computed from the standard deviations of CMB-derived component concentrations suggest that 10 to 20 randomly selected samples analyzed by INAA and SEM-EDX should be sufficient for most components. Although coarse particles were not analyzed by INAA in the present study, INAA data for Na in coarse particles would have been helpful to reduce the large uncertainty in the marine component based only on XRF data. However, it is appropriate that all samples were analyzed by XRF because XRF analysis is less expensive, and many analyzed samples were needed for the composite of CMB and MLR. Analysis of data subsets by MLR indicates that the sulfur-component was determined well with as few as 31 samples, but the vehicle-component required more than 50 samples to obtain adequate statisitcal precision (see Table 16).

Analysis of sulfate collected in dichotomous samplers was of little value in the present study other than to confirm that XRF could be used to measure S in sulfate. In future studies, it would be more useful to collect samples with annular denuder systems so that the nitrate volatilization problem can be avoided and both gaseous and particulate S and N compounds can be analyzed[29].

In the Philadelphia study, two dichotomous samplers were used to collect samples for XRF and SEM analyses. The use of two dichotomous samplers is not only expensive, but the resulting fine fraction samples are unsuitable for analysis by SEM. The modified dichotomous sampler shown in this report provides a way to use one device to collect both fine and coarse particles that can be analyzed by XRF, INAA and SEM.

The abundance of Pb in vehicle exhaust derived by CMB-MLR agreed with predictions of a comprehensive emissions model. If the model and its parameters were fully validated, it could be used instead of an expensive set of field measurements to derive the Pb abundance. However, not all parameters in that model have been validated, and the model does not include particulate mass resulting from condensation of exhaust gasses in the atmosphere. Until the model is validated for use with CMB, a composite of CMB and MLR will be needed to determine the Pb abundance.

REFERENCES

1. R. K. Stevens, T. G. Pace. Overview of the Mathematical and Empirical Receptor Models Workshop (Quail Roost II). **Atmos. Environ. 18** (1984) 1499.

2. P. K. Hopke. Receptor Modeling in Environmental Chemistry. Wiley, New York, NY (1985).

3. T. G. Pace. Ed. Receptor Methods for Source Apportionment. Air Pollution Control Association, Pittsburgh, PA (1986).

4. PM_{10} SIP Development Guideline. EPA-450/2-86-001, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC (1987).

5. Receptor Model Technical Series, Volume III (Revised), CMB User's Manual (Version 6.0). EPA-450/4-83-01R, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC (1987).

6. Protocol for Applying and Validating the CMB Model. EPA-450/4-87-010, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC (1987).

7. Protocol for Reconciling Differences Among Receptor and Dispersion Models. EPA-450/4-87-008, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC (1987).

8. T. G. Dzubay, R. K. Stevens, G. E. Gordon, I. Olmez, A. E. Sheffield, W. J. Courtney. A Composite Receptor Method Applied To Philadelphia Aerosol. **Environ. Sci. Technol. 22** (1988) 46.

9. G. E. Gordon, W. R. Pierson, J. M. Daisey, P. J. Lioy, J. A. Cooper, J. G. Watson, G. R. Cass. Considerations for Design of Source Apportionment Studies. **Atmos. Environ. 18** (1984) 1567.

10. I. Olmez, A. E. Sheffield, G. E. Gordon, J. E. Houck, L. C. Pritchett, J. A. Cooper, T. G. Dzubay, R. L. Bennett. Compositions of Particles from Selected Sources in Philadelphia for Receptor Modeling Applications. **J. Air Pollut. Control Assoc.**, (submitted).

11. S. A. Batterman, T. G. Dzubay, R. E. Baumgardner. Development of Crustal Profiles for Receptor Modeling. **Atmos. Environ.** (in press).

12. S. W. Rheingrover, G. E. Gordon. Wind-Trajectory Method for Determining Compositions of Particles from Major Air Pollution Sources. **Aerosol Sci. Technol. 8** (1988) 29.

13. J. E. Core, J. J. Shah, J. A. Cooper. Receptor Model Source Composition Library. EPA-450/4-85-002, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC, (1984).

14. Y. Mamane, T. G. Dzubay. Fly Ash Concentrations in Philadelphia Aerosol Determined by Electron Microscopy. **Water, Air, and Soil Pollut.** (in press).

15. T. G. Dzubay, Y. Mamane. Use of Electron Microscopy Data in Receptor Models for PM-10. **Atmos. Environ.** (submitted).

16. J. E. Core. Philadelphia Airshed Aerosol Study Summer, 1982: Sampling Site Characterization and Source Inventory Survey. NEA, Inc., Beaverton, OR, (1982) unpublished.

17. B. Y. H. Liu, D. Y. H. Pui, K. L. Rubow. Characteristics of Air Sampling Filter Media. In Aerosols in the Mining and Industrial Work Environments, Vol. 3. V. A. Marple, B. Y. H. Liu, eds. Ann Arbor Science, Ann Arbor, MI, (1983) pp 989-1038.

18. T. G. Dzubay, R. K. Barbour. A Method to Improve the Adhesion of Aerosol Particles on Teflon Filters. **J. Air Pollut. Control Assoc. 33** (1983) 692.

19. J. M. Jaklevic, R. C. Gatti, F. S. Goulding, B. W. Loo, A. C. Thompson. Aerosol Analysis for the Regional Air Pollution Study. EPA-600/4-81-006, Atmospheric Sciences Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, NC. (1981).

20. A. C. Thompson, J. M. Jaklevic, B. H. O'Connor, C. M. Morris. X-Ray Powder Diffraction System for Chemical Speciation of Particulate Aerosol Samples. **Nuclear Instr. and Methods 198** (1982) 539.

21. R. Otto, J. Jaklevic. The Use of X-Ray Powder Diffractometry in Combination with SEM and Microencapsulation for Studying the Physico-Chemical Transformations of Crystalline Particles on Teflon Filters. LBL-21379, Lawrence Berkeley Laboratory, Berkeley, CA.

22. J. M. Jaklevic, R. C. Gatti, F. S. Goulding, B. W. Loo. A β-Gauge Method Applied to Aerosol Samples. **Environ. Sci. Technol. 15** (1981) 680.

23. W. J. Courtney, R. W. Shaw, T. G. Dzubay. Precision and Accuracy of a β Gauge for Aerosol Mass Determinations. **Environ. Sci. Technol. 16** (1982) 236.

24. M. S. Germani, I. Gokmen, A. C. Sigleo, G. S. Kowalczyk, I. Olmez, A. Small, D. L. Anderson, M. P. Failey, M. C. Gulovali, C. E. Choquette, E. A. Lepel, G. E. Gordon, W. H. Zoller. Concentrations of Elements in the National Bureau of Standards Bituminous Coal Standard Reference Materials. **Anal. Chem. 52** (1980) 240.

25. R. K. Stevens. Sampling and Analysis Methods for use in Source Apportionment Studies to Determine Impact of Wood Burning on Fine Particle Mass. **Environ. International 11** (1985) 271.

26. R. K. Stevens, T. G. Dzubay, G. Russwurm, D. Rickel. Sampling and Analysis of Atmospheric Sulfates and Related Species. **Atmos. Environ. 12** (1978) 55.

27. T. G. Dzubay, R. K. Stevens, C. W. Lewis, D. H. Hern, W. J. Courtney, J. W. Tesch, M. A. Mason. Visibility and Aerosol Composition in Houston, Texas. **Environ. Sci. Technol. 16** (1982) 514.

28. W. John, S. M. Wall, J. L. Ondo. A New Method for Nitric Acid and Nitrate Aerosol Measurement Using the Dichotomous Sampler. **Atmos. Environ.** (in press).

29. T. L. Vossler, R. K. Stevens, R. J. Paur, R. E. Baumgardner, J. P. Bell. Evaluation of Improved Inlets and Annular Denuder Systems to Measure Inorganic Air Pollutants. **Atmos. Environ.** (in press).

30. T. G. Dzubay, R. K. Stevens, L. W. Richards. Composition of Aerosols over Los Angeles Freeways. **Atmos. Environ. 13** (1979) 653.

31. G. S. Kowalczyk, C. E. Choquette, G. E. Gordon. Chemical Element Balances and Identification of Air Pollution Sources in Washington, D. C. **Atmos. Environ. 12** (1978) 1143.

32. J. G. Watson, J. A. Cooper, J. J. Huntzicker. The Effective Variance Weighting for Least Squares Calculations Applied to the Mass Balance Receptor Model. **Atmos. Environ. 18** (1984) 1347.

33. S. N. Chang, P. K. Hopke, G. E. Gordon, S. W. Rheingrover. **Aerosol Sci. Technol. 8** (1988) 63.

34. W. R. Pierson, W. W. Brachaczek. Particulate Matter Associated with Vehicles on the Road. II. **Aerosol Sci. Technol. 2** (1983) 1.

35. A Guide to the Use of Factor Analysis and Multiple Regression Techniques in Source Apportionment. EPA-450/4-85-007, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC (1985).

36. C. W. Lewis, R. E. Baumgardner, R. K. Stevens, G.M. Russwurm. Receptor Modeling Study of Denver Winter Haze. **Environ. Sci. Technol. 20** (1986) 1126.

37. W. J. Dixon. BMDP Statistical Software. University of California Press, Berkeley, CA (1983).

38. R. C. Henry. Stability Analysis of Receptor Models that Use Least Squares Fitting. In Receptor Models Applied to Contemporary Pollution Problems. S. Dattner, P. Hopke, eds. Air Pollution Control Assoc., Pittsburgh, PA (1982), p 141-157.

39. Handbook of Chemistry and Physics. R. C. Weast, ed. CRC Press Inc., Cleveland, Ohio (1976) p. F199.

40. I. N. Tang. Deliquescence Properties and Particle Size Change of Hygroscopic Aerosols. In Generation of Aerosols and Facilities for Exposure Experiments. K. Willeke, ed. Ann Arbor Science, Ann Arbor, MI.

(1980), p 153-167.

41. Size Specific Total Particulate Emission Factors for Mobile Sources. EPA 460/3-85-005, Office of Mobile Sources, U. S. Environmental Protection Agency, Ann Arbor, MI (1985).

42. A Program to Calculate Size Specific Particulate Emissions for Mobile Sources — A User's Guide, EPA 460/3-85-007, Office of Mobile Sources, U. S. Environmental Protection Agency, Ann Arbor, MI (1985).

43. G. D. Thurston, J. D. Spengler. A Quantitative Assessment of Source Contributions to Inhalable Particulate Matter Pollution in Metropolitan Boston. **Atmos. Environ. 19** (1985) 9.

44. G. T. Wolff, P. E. Korsog. Estimates of the Contributions of Sources to Inhalable Particulate Concentrations in Detroit. **Atmos. Environ. 19** (1985) 1399.

45. W. R. Pierson, W. W. Brachaczek. Particulate Matter Associated with Vehicles on the Road. **Soc. Auto. Eng. 760039** (1976) 1.

46. Y. Mamane, T. G. Dzubay. Dichotomous Samplers Modified for Use with Electron Microscopy. **Aerosol Sci. Technol.** (to be submitted).

APPENDIX A

EXAMPLE OF TYPICAL DATA STORED ON DISKETTE*

```
1982 PHILADELPHIA STUDY: XRF, INAA, IC, PYROLYSIS, AND MET DATA FOR SITE 12
HEADER    12.00 714.18 719.00 195.75 153.00  31.00
     .00   46.00  54.00    .00    .00   2.40  24.00  83.00   4.50
NO3 IC        .0  160.0  310.0  161.5
SO4 IC   19323.0 1385.5  527.0  302.3
NH4 IC    6695.0  475.6 -663.0   93.4
 VC PYR   3091.0 1023.1  138.0 1000.0
NVC PYR   2184.0  160.8   36.0   50.1
MASS BET39390.1 3126.2 8034.6 2788.6
AL   XRF    23.1   35.8  337.4  111.2
SI   XRF    91.5   20.9 1215.9  292.9
S    XRF  6514.9  442.5  330.5  209.6
CL   XRF    -2.4    4.8   11.7    4.7
K    XRF    46.1    3.9   96.7   14.2
CA   XRF    19.1    2.0  167.2   14.9
TI   XRF    -2.4    8.5   53.8   10.8
V    XRF     7.3    4.2   14.3    4.5
CR   XRF     3.3    2.9    2.3    2.9
MN   XRF     9.4    2.4    5.7    2.4
FE   XRF    62.0    5.3  321.4   24.7
NI   XRF     3.3    1.1    2.9    1.1
CU   XRF     -.4    2.0   -3.5    1.9
ZN   XRF    19.8    2.1    3.6    1.5
SE   XRF      .8     .6     .3     .5
BR   XRF    21.7    1.6   12.9    1.2
SR   XRF      .4     .6     .9     .6
ZR   XRF     -.8    3.0    3.2    2.8
CD   XRF     5.8    2.7    3.1    2.4
SN   XRF     6.0    3.5    3.9    3.1
SB   XRF     4.3    3.9   -1.6    3.4
PB   XRF   211.2   13.1   35.7    4.2
NA   INAA   77.1    8.4
AL   INAA   43.6    5.3
S    INAA 3985.8 1189.0
CL   INAA   30.0   12.0
K    INAA   52.8    5.3
CA   INAA   21.8   10.9
SC*  INAA    9.5    1.0
TI   INAA     .0     .0
V    INAA    6.2     .6
CR   INAA     .8     .1
MN   INAA    3.3     .6
FE   INAA   73.9    7.4
CO*  INAA   72.8   14.8
CU   INAA     .0     .0
ZN   INAA   19.0    2.1
GA*  INAA   83.4   25.3
AS*  INAA  295.6   84.4
SE*  INAA 1435.6  147.8
BR   INAA   15.4    1.6
MO*  INAA  506.7  158.3
AG*  INAA   90.8   31.7
CD   INAA    2.5     .8
IN*  INAA    9.3    3.7
SB   INAA     .9     .1
I *  INAA 1393.3  348.3
CS*  INAA   19.0    5.3
LA*  INAA  327.2   42.2
CE*  INAA  390.6   42.2
SM*  INAA   30.6    3.2
HF*  INAA     .0     .0
W *  INAA   85.5   22.2
AU*  INAA     .6     .3
TH*  INAA     .0     .0
```

*Example pertains to site 12 sample that began July 14, 1982 (Julian day 195) at 1800 hours and had duration of 719 minutes. Wind $\theta = 153^\circ$, and $\delta\theta = 31^\circ$.

APPENDIX B1

XPD AND XRF RESULTS FOR FINE PARTICLE SAMPLE COLLECTED AT SITE 28 FOR THE 12-HOUR PERIOD BEGINNING AT 1800 ON AUGUST 9, 1982

Analysis Date =26-OCT-84 File = PL134 X-Ray Flux =0.8050
#247921F PHILADELPHIA, PA. 31-JUL-83

Standard	# Lines Found/Poss Major	Total	Normalization Factor	Error	Calb Fact	Concentration us/cm2	+-us/cm2
1*Mascagnite	1 1	15 15	23.21	0.11	0.59	80.633	24.193
2*Teflon	1 1	4 9	34.85	0.47	0.00	0.000	0.000
3*Lead Amm Sulfate	2 2	9 15	3.34	0.09	2.32	2.947	0.888
4*MASCAGNITE 2ND-SET	2 2	9 15	1.29	0.05	0.00	0.000	0.000
5*Biotite	1 2	4 10	1.94	0.21	1.60	2.485	0.793
6*Senarmontite-Sb203	1 1	2 8	1.96	0.08	16.31	0.246	0.075

Total Crystalline Mass = 86.311 us/cm2

Beta Mass = 108.821 us/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	4987.			
Li	1.			
N	17284.			
O	40956.			
F	27.			
Na	11.			
Mg	122.			
Al	190.	114.	-76.	167.0
Si	426.	572.	146.	74.4
P	0.	11.	11.	0.0
S	20004.	16573.	-3430.	120.7
K	169.	225.	56.	75.0
Ca	16.	169.	154.	9.3
Ti	51.	477.	426.	10.7
V	0.	144.	144.	0.0
Cr	0.	15.	15.	0.0
Mn	5.	21.	16.	24.9
Fe	454.	523.	69.	86.8
Ni	0.	65.	65.	0.0
Zn	0.	60.	60.	0.0
Se	0.	5.	5.	0.0
Br	0.	71.	71.	0.0
Rb	0.	1.	1.	0.0
Cd	0.	3.	3.	0.0
Sn	0.	1.	1.	0.0
Sb	206.	504.	299.	40.8
Pb	1402.	714.	-688.	196.4

Sample Attenuation 0.59% from XPD and 0.43% from XRF

APPENDIX B2

XPD AND XRF RESULTS FOR COARSE PARTICLE SAMPLE COLLECTED AT SITE 28 FOR THE 12-HOUR PERIOD BEGINNING AT 1800 ON AUGUST 9, 1982

Analysis Date =26-OCT-84 File = PL135 X-Ray Flux =0.8050
#147921C PHILADELPHIA, PA. 31-JUL-83

Standard	# Lines Found/Poss Major	Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Teflon	1 1	4 9	38.94	0.34	0.00	0.000	0.000
2*Senarmontite-Sb203	1 1	2 8	3.24	0.06	16.31	0.407	0.122
3*Quartz	1 1	1 8	1.31	0.06	1.98	1.354	0.411
4*Anatase -TiO2	1 1	1 6	0.74	0.08	2.06	0.736	0.235
5*Ankerite	1 1	1 4	0.43	0.07	0.85	1.034	0.353
6*Calcite	1 1	1 9	0.63	0.09	1.77	0.730	0.242

Total Crystalline Mass = 4.262 ug/cm2

Beta Mass = 13.394 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
C	205.			
O	1909.			
Mg	35.			
Al	0.	253.	253.	0.0
Si	634.	858.	223.	73.9
P	0.	57.	57.	0.0
S	0.	872.	872.	0.0
Cl	0.	60.	60.	0.0
K	0.	132.	132.	0.0
Ca	488.	207.	-281.	236.0
Ti	441.	413.	-28.	106.8
V	0.	8.	8.	0.0
Cr	0.	3.	3.	0.0
Mn	12.	7.	-5.	164.5
Fe	197.	470.	274.	41.8
Ni	0.	13.	13.	0.0
Zn	0.	16.	16.	0.0
As	0.	1.	1.	0.0
Br	0.	19.	19.	0.0
Rb	0.	1.	1.	0.0
Sr	0.	2.	2.	0.0
Cd	0.	6.	6.	0.0
Sn	0.	5.	5.	0.0
Sb	340.	255.	-85.	133.5
Ba	0.	17.	17.	0.0
Pb	0.	54.	54.	0.0

Sample Attenuation 0.07% from XPD and 0.11% from XRF

APPENDIX B3

XPD AND XRF RESULTS FOR FINE PARTICLE SAMPLE COLLECTED AT SITE 12
FOR THE 12-HOUR PERIOD BEGINNING AT 0600 ON AUGUST 9, 1982

Aalysis Date =20-NOV-84 File = PL042 X-Ray Flux =0.9120
247824F PHILADELPHIA, PA. 28-JUN-83

Standard	# Lines Major	Found/Poss Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Mascagnite	1 1	15 15	21.09	0.10	0.59	64.672	19.404
2*Mascagnite-Prefrd Or	1 1	9 11	44.66	0.20	11.50	7.026	2.108
3 Anglesite PbSO4	1 1	8 15	6.74	0.08	2.05		
4*Teflon	1 1	4 9	11.76	0.48	0.00	0.000	0.000
5*Lead Amm Sulfate	2 2	11 15	2.97	0.09	2.32	2.313	0.697
6*MASCAGNITE 2ND-SET	1 2	7 15	2.56	0.08	0.00	0.000	0.000
7*KOKTAITE AMM-CA-SULF	1 1	3 7	3.03	0.12	1.00	5.483	1.660

Total Crystalline Mass = 79.494 ug/cm2

Beta Mass = 138.971 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	4617.			
N	15884.			
O	38153.			
Al	0.	429.	429.	0.0
Si	0.	922.	922.	0.0
P	0.	30.	30.	0.0
S	18970.	18953.	-17.	100.1
K	0.	418.	418.	0.0
Ca	769.	361.	-407.	212.8
Ti	0.	98.	98.	0.0
V	0.	124.	124.	0.0
Cr	0.	14.	14.	0.0
Mn	0.	41.	41.	0.0
Fe	0.	644.	644.	0.0
Ni	0.	97.	97.	0.0
Cu	0.	32.	32.	0.0
Zn	0.	285.	285.	0.0
Se	0.	6.	6.	0.0
Br	0.	82.	82.	0.0
Sr	0.	3.	3.	0.0
Sn	0.	31.	31.	0.0
Sb	0.	4.	4.	0.0
Pb	1100.	1081.	-20.	101.8

Sample Attenuation 0.52% from XPD and 0.47% from XRF

APPENDIX B4

XPD AND XRF RESULTS FOR COARSE PARTICLE SAMPLE COLLECTED AT SITE 12
FOR THE 12-HOUR PERIOD BEGINNING AT 0600 ON AUGUST 9, 1982

Analysis Date =26-OCT-84 File = PL041 X-Ray Flux =0.9150
#147824C PHILADELPHIA, PA. 28-JUN-83

Standard		# Lines Major	Found/Poss Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Teflon		1 1	4 9	44.38	0.50	0.00	0.000	0.000
2*Quartz		1 1	6 8	9.05	0.09	1.98	8.230	2.470
3*Muscovite		1 1	4 15	3.10	0.29	0.40	13.975	4.392
4*Dolomite		1 1	2 6	2.29	0.07	1.53	2.697	0.813
5*Magnetite		1 1	2 3	0.88	0.09	1.64	0.965	0.306
6*Calcite		1 1	2 9	1.43	0.10	1.77	1.457	0.449
7*Mascagnite		1 1	3 15	0.77	0.12	0.59	2.353	0.796
8*Halite	NaCl	1 1	2 3	1.21	0.36	3.15	0.694	0.292
9*Gypsum	CaSO4-2H2	2 2	2 15	0.41	0.09	0.61	1.207	0.458

Total Crystalline Mass = 31.579 ug/cm2

Beta Mass = 63.128 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	243.			
Li	13.			
C	524.			
N	499.			
O	15260.			
F	34.			
Na	374.			
Mg	422.			
Al	2348.	1755.	-594.	133.8
Si	6924.	5872.	-1052.	117.9
P	0.	124.	124.	0.0
S	793.	1082.	290.	73.2
Cl	421.	571.	150.	73.7
K	1052.	621.	-432.	169.6
Ca	1536.	2221.	685.	69.2
Ti	32.	175.	143.	18.4
V	0.	29.	29.	0.0
Cr	49.	9.	-40.	553.0
Mn	10.	43.	33.	23.4
Fe	924.	2077.	1153.	44.5
Ni	0.	33.	33.	0.0
Cu	0.	55.	55.	0.0
Zn	0.	204.	204.	0.0
Br	0.	67.	67.	0.0
Rb	0.	1.	1.	0.0
Sr	0.	15.	15.	0.0
Sn	0.	7.	7.	0.0
Sb	0.	47.	47.	0.0
Ba	82.	18.	-64.	446.8
Pb	0.	324.	324.	0.0

Sample Attenuation 0.29% from XPD and 0.36% from XRF

APPENDIX B5

XPD AND XRF RESULTS FOR FINE PARTICLE SAMPLE COLLECTED AT SITE 12 FOR THE 12-HOUR PERIOD BEGINNING AT 0600 ON AUGUST 13, 1982

Analysis Date =26-OCT-84 File = PL058 X-Ray Flux =0.8930
#247832F PHILADELPHIA, PA. 4-JUL-83

Standard	# Lines Major	Found/Poss Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Teflon	1 1	4 9	109.81	0.52	0.00	0.000	0.000
2*Mascagnite	1 1	14 15	4.49	0.10	0.59	14.061	4.230
3*Mascagnite-Prefrd Or	1 1	5 11	23.73	0.16	11.50	3.812	1.144
4*Biotite	2 2	4 10	1.60	0.12	1.60	1.846	0.571
5*Senarmontite-Sb203	1 1	3 8	0.80	0.06	16.31	0.091	0.028

Total Crystalline Mass = 19.810 ug/cm2

Beta Mass = 42.760 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	1097.			
Li	1.			
N	3789.			
O	9417.			
F	20.			
Na	8.			
Mg	90.			
Al	141.	112.	-30.	126.7
Si	316.	313.	-3.	100.9
P	0.	53.	53.	0.0
S	4338.	4793.	456.	90.5
K	126.	404.	278.	31.1
Ca	12.	213.	201.	5.5
Ti	38.	41.	3.	92.6
V	0.	24.	24.	0.0
Mn	4.	28.	24.	13.9
Fe	337.	355.	18.	95.0
Ni	0.	17.	17.	0.0
Zn	0.	124.	124.	0.0
Se	0.	5.	5.	0.0
Br	0.	75.	75.	0.0
Rb	0.	2.	2.	0.0
Sr	0.	1.	1.	0.0
Sb	76.			
Pb	0.	535.	535.	0.0

Sample Attenuation 0.14% from XPD and 0.15% from XRF

APPENDIX B6

XPD AND XRF RESULTS FOR COARSE PARTICLE SAMPLE COLLECTED AT SITE 12 FOR THE 12-HOUR PERIOD BEGINNING AT 0600 ON AUGUST 13, 1982

Analysis Date =26-OCT-84 File = PL057 X-Ray Flux =0.8960
#147832C PHILADELPHIA, PA. 3-JUL-83

Standard	# Lines Found/Poss Major	Total	Normalization Factor	Error	Calb Fact	Concentration ug/cm2	+-ug/cm2
1*Teflon	1 1	4 9	101.75	0.41	0.00	0.000	0.000
2*Quartz	1 1	5 8	6.35	0.07	1.98	5.897	1.770
3*Muscovite	1 1	4 15	1.86	0.31	0.40	8.563	2.939
4*Dolomite	1 1	2 6	1.31	0.07	1.53	1.576	0.480
5*Calcite	1 1	2 9	1.55	0.08	1.77	1.613	0.491
6*PLAGIOCLASE(ALBITE)	2 2	2 15	1.89	0.07	1.00	3.488	1.054

Total Crystalline Mass = 21.137 ug/cm2

Beta Mass = 50.862 ug/cm2

ELEMENT	XPD ng/cm2	XRF ng/cm2	Difference ng/cm2	%
H	45.			
Li	8.			
C	396.			
O	10428.			
F	21.			
Na	205.			
Mg	250.			
Al	1943.	1252.	-691.	155.2
Si	5554.	3797.	-1757.	146.3
P	0.	182.	182.	0.0
S	0.	519.	519.	0.0
Cl	0.	234.	234.	0.0
K	674.	1064.	390.	63.3
Ca	1330.	1878.	548.	70.8
Ti	20.	74.	54.	27.5
V	0.	16.	16.	0.0
Cr	30.	4.	-26.	832.3
Mn	6.	35.	29.	17.5
Fe	152.	1351.	1199.	11.2
Ni	0.	7.	7.	0.0
Zn	0.	176.	176.	0.0
Se	0.	1.	1.	0.0
Br	0.	33.	33.	0.0
Rb	0.	1.	1.	0.0
Sr	2.	6.	5.	27.4
Sn	0.	6.	6.	0.0
Sb	0.	9.	9.	0.0
Ba	51.	49.	-2.	104.6
Pb	0.	114.	114.	0.0

Sample Attenuation 0.17% from XPD and 0.24% from XRF

APPENDIX C

SOURCE SIGNATURES USED FOR FINE PARTICLE CMB

	1		2		4		5		6		8	
	Dust	±	Soil	±	Oil-Sk	±	Oil-Ed	±	Oil-Av	±	Paint	±
NO3	2.140	3.22	7.160	3.37	.000	.00	.000	.00	.000	.00	.000	.00
SO4	5.500	2.10	2.690	1.80	45.000	7.00	40.000	4.00	42.500	3.50	.000	.00
NH4	.000	.00	.000	.00	3.700	1.70	3.500	1.60	3.600	1.65	.000	.00
VC	10.200	3.89	4.130	3.72	.750	.63	2.700	1.20	1.700	1.00	.000	.00
NVC	1.450	.37	.520	.29	.220	.17	7.700	1.50	3.960	3.74	.000	.00
MASS	100.00	26.0	100.00	18.0	100.00	.0	100.00	.0	100.00	.0	100.00	.0
AL	2.210	1.39	8.800	2.25	.940	.08	.450	.09	.695	.24	3.140	.90
SI	8.460	2.77	14.820	3.47	2.600	.40	1.900	.60	2.250	.50	.220	.67
S	.100	.16	.130	.18	13.000	1.00	11.000	2.00	12.000	1.50	.000	.00
CL	.030	.06	.030	.06	.000	.00	.019	.009	.010	.01	.000	.00
K	.790	.26	1.140	.27	.210	.03	.160	.05	.185	.04	2.910	1.34
CA	1.190	.54	.620	.36	2.300	1.00	3.600	1.00	2.950	.90	6.720	1.12
TI	.360	.16	.550	.19	.120	.02	.040	.044	.080	.05	22.400	1.12
V	.000	.09	.010	.10	2.000	.30	1.150	.30	1.575	.40	.000	.00
CR	.060	.03	.040	.02	.023	.007	.024	.001	.024	.006	.000	.00
MN	.090	.03	.070	.03	.021	.005	.038	.004	.030	.009	.000	.00
FE	6.080	2.71	7.880	1.64	1.700	.40	1.600	.20	1.650	.30	15.900	.45
NI	.020	.02	.020	.02	1.900	.20	1.500	.50	1.700	.35	.090	.02
CU	.010	.04	.010	.04	.110	.05	.098	.032	.104	.04	.110	.04
ZN	.060	.05	.020	.03	.780	.30	1.300	.30	1.040	.30	.520	.49
SE	.000	.01	.000	.01	.002	.001	.003	.001	.002	.001	.090	.03
BR	.010	.01	.000	.01	.004	.002	.009	.006	.007	.004	.900	.67
SR	.020	.02	.020	.01	.028	.007	.016	.005	.022	.006	.004	.067
ZR	.010	.04	.030	.04	.010	.012	.014	.018	.012	.017	.000	.00
CD	.000	.10	.000	.10	.000	.00	.000	.00	.000	.00	.200	.07
SN	.000	.10	.000	.10	.020	.008	.032	.023	.026	.015	.000	.00
SB	.000	.10	.000	.10	.102	.009	.037	.041	.070	.031	.000	.00
PB	.310	.32	.040	.05	1.000	.20	1.800	.60	1.400	.40	.670	2.02
NA	2.830	2.83	2.830	2.83	3.300	.80	3.000	.80	3.150	.70	.000	.00
AL	2.210	1.39	8.800	2.25	.940	.08	.450	.09	.695	.24	3.140	.90
SC*	.500	1.00	.500	1.00	.047	.002	.017	.002	.032	.014	.000	.00
V	.000	.09	.010	.10	2.000	.30	1.150	.30	1.575	.40	.000	.00
CR	.060	.03	.040	.02	.023	.007	.024	.001	.024	.004	.000	.00
MN	.090	.03	.070	.03	.021	.005	.038	.004	.030	.009	.000	.00
CO*	2.300	4.60	2.300	4.60	110.00	20.0	79.00	15.0	94.50	17.5	.000	.0
AS*	.500	1.00	.500	1.00	5.000	1.60	3.300	.60	4.150	1.00	.000	.00
SE*	90.000	.02	.010	.02	2.300	.70	2.600	.90	2.450	.70	.000	.00
MO*	1.500	3.00	1.500	3.00	150.00	30.0	93.00	21.00	121.50	30.0	.000	.00
AG*	.010	.02	.010	.02	.000	.00	.000	.00	.000	.00	.000	.00
CD	.000	.10	.000	.10	.000	.00	.000	.00	.000	.00	.200	.07
IN*	.010	.02	.010	.02	.000	.00	.000	.00	.000	.00	.000	.00
I *	.030	.06	.030	.06	.000	.00	.000	.00	.000	.00	.000	.00
CS*	.700	1.40	.700	1.40	.000	.00	.000	.00	.000	.00	.000	.00
LA*	1.800	3.60	1.800	3.60	45.000	3.00	13.000	3.00	29.00	16.00	.000	.00
CE*	4.600	9.20	4.600	9.20	36.000	2.00	8.900	2.30	22.500	14.00	.000	.00
SM*	.650	1.30	.650	1.30	2.050	.15	.370	.07	1.210	.80	.000	.00
W *	6.900	13.80	6.900	13.80	.000	.00	6.000	.50	.000	.00	.000	.00
AU*	.001	.00	.001	.00	.000	.00	.005	.002	.003	.003	.000	.00
TH*	1.200	2.40	1.200	2.40	.000	.00	.190	.05	.095	.10	.000	.00

*Data without asterisk are in Percent; data with asterisk are in percent x 1000.

APPENDIX C CONTINUED

SOURCE SIGNATURES USED FOR FINE PARTICLE CMB

	9		11		12		13		14		15	
	SoilMed	±	Incin	±	Veh Exh	±	Sb	±	IncComp	±	Earth	±
NO3	.100	.04	.000	.00	.900	.30	.000	.00	.000	.00	.000	.00
SO4	.100	.04	6.800	2.30	5.700	2.00	.660	.33	.000	.00	.000	.00
NH4	.000	.00	.360	.07	.000	.00	.049	.035	.000	.00	.000	.00
VC	4.400	1.70	.570	.26	35.000	18.00	.940	.49	.000	.00	.000	.00
NVC	.600	.40	3.500	.20	40.600	21.00	.099	.024	.000	.00	.000	.00
MASS	100.00	.0	100.00	.0	100.00	10.0	100.00	.0	100.00	.0	100.00	20.0
AL	9.500	.10	.250	.10	.000	.00	.100	.12	1.170	.59	8.130	1.63
SI	26.600	1.40	1.700	.30	.000	.00	.000	.00	.000	.00	27.720	5.54
S	.090	.04	2.900	.80	1.760	1.10	1.280	.07	4.300	7.50	.052	.01
CL	.070	.05	29.000	5.00	1.100	.60	.012	.019	22.300	4.30	.031	.006
K	.920	.33	7.600	2.30	.000	.00	.000	.00	5.00	10.00	2.590	.52
CA	1.800	.40	.230	.10	.000	.00	.000	.00	.767	1.33	3.630	.73
TI	1.000	.10	.030	.015	.000	.00	.000	.00	.193	.127	.440	.09
V	.024	.00	.001	.001	.000	.00	.001	.00	.000	.001	.015	.003
CR	.024	.00	.010	.003	.002	.001	.000	.00	.036	.023	.020	.004
MN	.160	.07	.019	.004	.060	.03	.001	.00	.083	.062	.100	.02
FE	5.300	.60	.220	.05	.280	.14	.000	.00	.627	.286	5.000	1.00
NI	.007	.003	.029	.004	.002	.001	.014	.001	.014	.006	.008	.002
CU	.030	.02	.130	.05	.000	.00	.000	.00	.180	.017	.007	.002
ZN	.009	.003	10.400	.50	.100	.10	.000	.00	11.800	.35	.013	.003
SE	.000	.00	.004	.002	.000	.00	.000	.00	.000	.00	.000	.00
BR	.000	.00	.230	.08	2.600	1.30	.000	.00	.166	.097	.000	.00
SR	.000	.00	.009	.001	.000	.00	.000	.00	.000	.00	.030	.006
ZR	.000	.00	.000	.00	.000	.00	.000	.00	.025	.023	.022	.004
CD	.000	.00	.120	.07	.000	.00	.000	.00	.115	.047	.000	.00
SN	.000	.00	.670	.19	.000	.00	.000	.00	.885	.557	.004	.001
SB	.000	.00	.130	.10	.000	.00	78.000	4.00	.168	.078	.000	.00
PB	.011	.00	5.800	1.20	6.900	1.60	.170	.04	8.230	1.40	.002	.00
NA	1.500	.50	6.600	3.50	.600	.30	.000	.00	9.550	1.80	2.830	.57
AL	9.500	.10	.250	.10	.000	.00	.100	.12	1.170	.59	8.130	1.63
SC*	.000	.00	.011	.002	.000	.00	.000	.00	.000	.00	.500	.10
V	.024	.00	.001	.001	.000	.00	.001	.00	.000	.001	.015	.003
CR	.024	.00	.010	.003	.002	.001	.000	.00	.036	.023	.020	.004
MN	.160	.07	.019	.004	.060	.03	.001	.00	.083	.062	.100	.02
CO*	.000	.00	.370	.08	.000	.00	.000	.00	.000	.00	2.300	.46
AS*	.000	.00	6.400	3.40	.000	.00	.000	.00	20.000	4.00	.500	.10
SE*	.000	.00	4.200	1.60	.000	.00	.000	.00	.000	.00	.009	.002
MO*	.000	.00	24.000	13.00	.000	.00	.000	.00	.000	.00	1.500	.30
AG*	.000	.00	7.100	1.50	.000	.00	.000	.00	25.000	23.00	.010	.002
CD	.000	.00	.120	.07	.000	.00	.000	.00	.115	.047	.015	.003
IN*	.000	.00	.490	.14	.000	.00	.000	.00	.000	.00	.010	.002
I *	.000	.00	.000	.00	4.000	2.00	.000	.00	.000	.00	.030	.006
CS*	.000	.00	.590	.30	.000	.00	.000	.00	4.000	4.00	.700	.14
LA*	.000	.00	.110	.05	.000	.00	.000	.00	.000	.00	1.800	.36
CE*	.000	.00	.000	.00	.000	.00	.000	.00	.000	.00	4.600	.92
SM*	.000	.00	.000	.00	.000	.00	.000	.00	.000	.00	.650	.13
W *	.000	.00	.000	.00	.000	.00	.000	.00	.000	.00	6.900	1.38
AU*	.000	.00	.056	.027	.000	.00	.000	.00	.000	.00	.001	.00
TH*	.000	.00	.000	.00	.000	.00	.000	.00	.000	.00	1.200	.24

*Data without asterisk are in Percent; data with asterisk are in percent x 1000.

APPENDIX D

SIGNATURES USED FOR CMB ANALYSIS OF COARSE PARTICLES*

	1 OMIT		2 USE+		3 OMIT		4 OMIT		8 USE+	
	Dust	±	Soil	±	Coal	±	Earth	±	Marine	±
NO3	.380	.22	.760	.57	.000	.000	.000	.000	.000	.00
SO4	.800	.19	1.420	.52	2.400	.300	.000	.000	10.000	4.00
NH4	.000	.00	.000	.00	.150	.020	.000	.000	.000	.00
VC	6.560	1.06	1.900	.90	.000	.000	.000	.000	.000	.00
NVC	2.790	.49	.770	.20	2.000	.100	.000	.000	.000	.00
MASS	100.00	5.0	100.00	5.0	100.00	.00	100.00	20.00	100.00	.00
AL	2.880	.99	6.710	2.31	19.000	2.000	8.130	1.630	.000	.00
SI	14.730	3.26	26.080	6.03	18.500	2.800	27.720	5.544	.000	.00
S	.220	.15	.350	.14	.540	.070	.052	.010	3.300	1.30
CL	.030	.16	.030	.16	.110	.080	.031	.006	40.000	10.00
K	1.090	.16	1.550	.24	1.330	.080	2.590	.518	1.400	.20
CA	4.660	.55	1.710	.50	2.300	.500	3.630	.726	1.400	.20
TI	.660	.12	1.060	.19	1.400	.250	.440	.088	.000	.00
V	.010	.02	.020	.02	.044	.009	.015	.003	.000	.00
CR	.100	.03	.100	.03	.019	.001	.020	.004	.000	.00
MN	.140	.02	.070	.02	.022	.002	.100	.020	.000	.00
FE	10.550	2.44	6.430	.88	8.100	.400	5.000	1.000	.000	.00
NI	.050	.01	.040	.01	.032	.002	.008	.002	.000	.00
CU	.010	.04	.010	.04	.024	.001	.007	.001	.000	.00
ZN	.220	.04	.060	.02	.028	.002	.013	.003	.000	.00
SE	.000	.00	.000	.00	.002	.000	.000	.000	.000	.00
BR	.010	.00	.000	.00	.000	.000	.000	.000	.200	.05
SR	.030	.01	.020	.01	.157	.008	.030	.006	.000	.00
ZR	.020	.01	.030	.01	.039	.013	.022	.004	.000	.00
CD	.000	.04	.000	.05	.000	.000	.000	.000	.000	.00
SN	.000	.04	.000	.05	.000	.000	.004	.001	.000	.00
SB	.000	.04	.000	.05	.000	.000	.000	.000	.000	.00
PB	.700	.14	.060	.05	.026	.002	.002	.000	.000	.00

*Data are species abundances in percent.

APPENDIX D CONTINUED

SIGNATURES USED FOR CMB ANALYSIS OF COARSE PARTICLES*

	9 OMIT		11 USE		12 USE		13 USE		15 OMIT		16 USE
	SoilMed	±	Incin	±	Vehicl	±	Sb	±	IncComp	±	SO4
NO3	.000	.00	.000	.00	.900	.300	.000	.000	.000	.00	.0
SO4	.060	.06	12.000	3.00	3.100	1.800	2.100	1.000	.000	.00	100.
NH4	.000	.00	.000	.00	.000	.000	.000	.000	.000	.00	.0
VC	3.700	.70	2.500	2.40	43.000	22.000	.000	.000	.000	.00	.0
NVC	.700	.70	2.300	.50	37.000	18.000	.200	.300	.000	.00	.0
MASS	100.00	.0	100.00	.0	100.00	.00	100.00	.000	100.00	.00	100.
AL	8.900	.20	5.100	.60	.600	.800	.500	1.100	1.170	.59	.0
SI	27.000	1.40	8.600	2.00	1.100	.500	.000	.000	.000	.00	.0
S	.070	.05	3.200	.70	1.500	1.100	1.300	.100	4.300	7.50	33.0
CL	.000	.00	14.000	3.00	1.000	1.000	.990	.130	22.300	4.30	.0
K	.750	.16	4.500	.60	.340	.270	.000	.000	5.000	10.00	.0
CA	1.800	.20	10.000	2.00	1.200	1.100	.000	.000	.767	1.33	.0
TI	.700	.20	1.600	.20	.160	.160	1.000	.500	.193	.13	.0
V	.033	.00	.010	.00	.000	.000	.001	.003	.000	.00	.0
CR	.026	.00	.110	.050	.002	.001	.000	.000	.036	.02	.0
MN	.180	.05	.093	.01	.150	.090	.001	.001	.083	.06	.0
FE	5.500	.80	1.700	.30	1.200	.900	.000	.000	.627	.29	.0
NI	.007	.00	.110	.05	.010	.008	.012	.003	.014	.01	.0
CU	.030	.00	.080	.10	.080	.060	.000	.000	.180	.02	.0
ZN	.011	.00	4.300	3.70	.210	.140	.000	.000	11.800	.35	.0
SE	.000	.00	.006	.00	.000	.000	.000	.000	.000	.00	.0
BR	.000	.00	.120	.05	2.220	1.110	.023	.012	.166	.10	.0
SR	.000	.00	.031	.01	.010	.010	.000	.000	.000	.00	.0
ZR	.000	.00	.000	.00	.040	.040	.000	.000	.000	.00	.0
CD	.000	.00	.080	.03	.000	.000	.000	.000	.115	.05	.0
SN	.000	.00	.000	.00	.000	.000	.000	.000	.885	.58	.0
SB	.000	.00	.029	.02	.000	.000	75.000	13.000	.168	.08	.0
PB	.000	.00	1.700	.50	7.100	1.600	.110	.020	8.230	1.40	.0

*Data are species abundances in percent.

APPENDIX E. FINE PARTICLE CMB RESULTS FOR SITE 28

	time	θ	δθ	χ^2	M(Obs)	M(Cal)	Dust	Oil-Av	Paint	CatCr	Incin	Sb
1	714.2	153	31	.7	46496	1622	1134	482	-43	30	21	-1
2	715.1	142	35	.9	17359	1498	1273	116	70	24	14	2
3	715.2	171	10	1.9	13639	1489	650	671	-47	148	-7	74
4	716.1	224	25	4.4	46496	4939	1549	2036	71	638	304	341
5	716.2	222	20	3.1	39057	1858	960	589	16	231	-20	84
6	717.1	232	15	1.9	38437	2526	775	1293	12	377	18	51
7	717.2	219	16	4.0	20458	1075	28	526	53	224	-28	272
8	718.1	248	57	2.7	53295	3376	940	1168	50	734	56	429
9	718.2	237	14	2.8	49596	3048	768	508	168	191	-5	1419
10	719.1	268	30	1.1	44016	3015	1380	1251	68	170	78	68
11	719.2	263	18	1.3	37817	4167	1143	2431	45	259	165	123
12	720.1	338	78	1.8	31617	4276	1662	1905	62	131	459	57
13	720.2	5	24	1.5	19218	2230	308	419	44	29	1430	-1
14	721.1	13	22	1.5	8679	1699	888	263	-61	24	581	4
15	721.2	318	20	.8	20458	9610	1002	233	47	90	8232	6
16	722.1	315	18	1.7	19838	8391	743	394	73	37	7136	9
17	722.2	327	91	3.1	40916	4169	1440	570	43	781	1243	92
18	723.1	133	76	1.4	30997	3768	2634	559	-70	34	606	6
19	723.2	320	63	.9	28518	3102	1064	718	21	173	835	291
20	724.1	75	61	1.5	17505	1911	799	478	42	28	559	5
21	724.2	232	48	1.3	14817	1660	524	809	-10	128	53	155
22	725.1	243	23	.8	33557	3488	1331	1168	-37	362	342	323
23	725.2	226	14	1.4	39677	1882	598	757	74	290	84	79
24	726.2	318	45	1.2	41536	2356	1491	379	-21	122	383	1
25	727.1	79	101	.6	24763	3233	1982	659	-29	96	518	7
26	728.1	202	56	.7	53935	2126	916	665	56	161	286	41
27	728.2	311	23	.8	23558	1762	489	563	22	26	656	6
28	731.2	226	58	3.3	40193	1891	299	848	152	286	178	128
29	801.1	329	13	6.4	23498	889	418	173	47	100	148	3
30	801.2	298	25	1.1	25971	2760	938	547	156	284	747	89
31	802.1	286	41	2.0	32773	2952	1060	768	21	221	757	126
32	802.2	328	35	2.2	30300	2747	680	566	63	74	1355	8
33	803.1	3	17	1.1	24116	2402	1533	276	-39	11	623	-1
34	803.2	340	18	1.8	32773	2176	916	497	5	157	516	85
35	804.1	256	57	2.0	37101	3358	1052	674	127	399	995	112
36	804.2	211	16	1.6	40360	1798	969	488	-25	202	166	-2
37	805.1	239	17	3.5	64309	3229	1377	749	221	695	183	4
38	806.1	87	38	2.9	17397	1237	818	190	99	15	120	-4
39	806.2	96	31	4.6	6802	989	810	140	65	-72	50	-4
40	807.1	195	85	1.8	12367	1217	705	186	72	109	152	-6
41	807.2	227	17	3.3	6184	1161	650	298	127	71	18	-4
42	808.1	188	8	1.4	11749	1192	929	192	46	-1	23	3
43	808.2	183	48	1.7	19787	867	642	149	1	50	22	3
44	809.1	236	14	2.3	20406	1741	624	498	121	412	65	21
45	809.2	229	21	2.4	24422	2344	345	1155	409	329	-13	119
46	810.1	255	23	2.4	30300	2403	635	1294	75	184	208	8
47	810.2	327	35	.2	25971	3449	1432	834	-23	-1	1205	2
48	811.1	29	19	1.0	12367	2515	1360	480	6	11	659	-2
49	811.2	32	22	1.9	12986	2433	384	654	0	18	1385	-8
50	812.2	1	14	.6	21024	2294	1322	536	-27	90	384	-11
51	813.1	332	33	.2	12986	2896	1032	524	53	12	1275	0
Mean		211	34	1.9	28282	2651	969	673	48	180	691	90
Mean Unc.					3121	370	311	129	41	49	72	11

APPENDIX F. COARSE PARTICLE CMB RESULTS FOR SITE 28

	time	Θ	δΘ	Chi^2	M(Obs)	M(Cal)	Soil	Marine	Incin	Vehicl	Sb	SO4
1	714.2	153	31	.5	11950	9153	7108	0	33	745	5	1261
2	715.1	142	35	.2	8516	6650	5668	16	18	455	-2	494
3	715.2	171	10	1.1	10552	6714	5339	0	15	692	176	492
4	716.1	224	25	1.9	19048	14991	11133	0	51	979	1010	1818
5	716.2	222	20	.6	24757	20248	18464	22	-110	577	362	933
6	717.1	232	15	1.3	16634	9754	7696	0	48	390	77	1542
7	717.2	219	16	1.2	9276	4650	3159	0	-13	565	552	387
8	718.1	248	57	.5	19188	15037	12511	0	-15	337	927	1278
9	718.2	237	14	1.0	18170	10888	6505	0	-537	630	3596	694
10	719.1	268	30	3.0	14945	12190	10564	0	202	566	206	652
11	719.2	263	18	2.9	16700	10993	9019	0	238	406	379	951
12	720.1	338	78	3.8	22278	13924	11364	0	795	646	222	897
13	720.2	5	24	4.0	5041	3783	2377	72	71	956	8	298
14	721.1	13	22	1.0	9445	5382	4610	67	6	509	-1	190
15	721.2	318	20	.9	14736	10039	7280	515	125	1795	10	315
16	722.1	315	18	1.1	14802	11321	9537	361	58	942	4	420
17	722.2	327	91	1.7	16915	14937	12459	0	190	1632	358	299
18	723.1	133	76	3.6	13062	11199	9247	0	253	1251	24	423
19	723.2	320	63	4.0	11690	9340	7257	0	190	681	692	520
20	724.1	75	61	2.7	12992	8168	7266	0	187	417	5	293
21	724.2	232	48	.6	10920	6387	4922	13	109	716	400	226
22	725.1	243	23	2.5	10349	9593	7690	0	200	433	957	314
23	725.2	226	14	.7	12134	6271	4780	8	33	561	230	658
24	726.2	318	45	2.5	14119	7967	6431	0	178	570	3	785
25	727.1	79	101	1.7	19704	11722	10684	0	255	515	5	264
26	728.1	202	56	3.4	9516	6764	4313	0	143	726	138	1442
27	728.2	311	23	2.9	9491	3801	2314	0	69	354	2	1062
28	731.2	226	58	8.1	5695	4015	2441	0	45	499	327	703
29	801.1	329	13	2.7	6898	2908	2277	0	34	275	13	309
30	801.2	298	25	.8	3884	4992	3595	0	78	899	144	275
31	802.1	286	41	1.3	10331	10880	8622	0	270	1189	328	471
32	802.2	328	35	1.8	11141	5942	4790	0	234	557	6	355
33	803.1	3	17	1.4	5180	7363	6392	250	-648	965	5	398
34	803.2	340	18	3.0	8678	6525	4771	0	182	1014	191	368
35	804.1	256	57	3.9	14283	11544	9591	0	291	990	265	407
36	804.2	211	16	.6	7177	11446	10354	0	45	539	8	500
37	805.1	239	17	.1	20240	13948	12542	0	113	432	20	842
38	806.1	87	38	.0	11950	10710	9149	348	26	530	8	648
39	806.2	96	31	1.2	9202	7166	2995	3419	40	661	5	47
40	807.1	195	85	.5	12473	8904	6117	1990	1	531	-3	267
41	807.2	227	17	4.8	9817	5982	4173	1064	-36	624	0	157
42	808.1	188	8	.5	11987	11306	9604	1224	-101	382	-3	200
43	808.2	183	48	1.6	3431	3968	2319	779	-29	285	4	610
44	809.1	236	14	.3	2264	3195	2170	16	132	401	93	383
45	809.2	229	21	19.9	7477	3837	2550	0	181	325	169	611
46	810.1	255	23	.4	12243	6319	4962	0	226	467	21	643
47	810.2	327	35	.8	7740	5952	4794	0	264	644	-6	256
48	811.1	29	19	1.9	5863	5945	5040	207	-471	859	2	308
49	811.2	32	22	3.7	1391	2095	1403	63	-69	474	-7	232
50	812.2	1	14	2.2	7157	6473	4846	58	43	1423	-11	115
51	813.1	332	33	1.5	9654	6975	5709	151	-231	1115	-3	234
Mean				2.2	11433	8436	6684	209	67	689	234	554
Mean uncertainty					2790	1084	824	202	214	194	46	427

APPENDIX G

EXAMPLE OF RESULTS OF MLR ANALYSIS

```
BMDP9R - ALL POSSIBLE SUBSETS REGRESSION

PROGRAM CONTROL INFORMATION

TO SEE REMARKS AND A SUMMARY OF NEW FEATURES FOR
THIS PROGRAM, STATE NEWS. IN THE PRINT PARAGRAPH.

PROGRAM CONTROL INFORMATION

/PROBLEM TITLE=' MASSX VS SX & PBX FOR SITE 28'.
/INPUT    VARIABLES = 116.    CASES = 157.    UNIT = 14.
       FORMAT IS '(6F7.0/10(10F7.0/),10F7.0)'.
/VARIABLE NAMES ARE
  SITE,DATE,MIN,JDAY,ANGLE,DEV,NO3,SO4,NH4,VC,NVC,MASS,
  AL,SI,S,CL,K,CA,TI,V,CR,MN,FE,NI,CU,ZN,SE,BR,SR,ZR,CD,SN,SB,PB,
  NA,NAL,SC,NV,NCR,NMN,CO,AS,NSE,MO,AG,NCD,IN,I,CS,LA,CE,SM,W,AU,TH,X50,
  NO3X,SO4X,NH4X,VCX,NVCX,MASSX,ALX,SIX,SX,CLX,
  KX,CAX,TIX,VX,CRX,MNX,FEX,NIX,CUX,ZNX,
  SEX,BRX,SRX,ZRX,CDX,SNX,SBX,PBX,NAX,NALX,
  SCX,NVX,NCRX,NMNX,COX,ASX,NSEX,MOX,AGX,NCDX,
  INX,IX,CSX,LAX,CEX,SMX,WX,AUX,THX,X100,
  DUST,OIL,PAINT,CATCR,INCIN,SBROAST,ZNDBR,VDPB,NIDPB,ZNDPB.
    MINIMUM = 116*-9990.
/PRINT PAGESIZE=57.
/TRANSFORM  SX=SX/1000.  PBX=PBX/1000.  MASSX=MASSX/1000.
  USE = KASE NE 91 AND SITE EQ 28.
/REGRESS  DEPENDENT IS MASSX.  INDEPENDENT IS SX,PBX.
/END

PROBLEM TITLE IS
 MASSX VS SX & PBX FOR SITE 28

NUMBER OF VARIABLES TO READ IN. . . . . .     116
NUMBER OF VARIABLES ADDED BY TRANSFORMATIONS. .     0
TOTAL NUMBER OF VARIABLES . . . . . .     116
NUMBER OF CASES TO READ IN. . . . . .     157
CASE LABELING VARIABLES . . . . . .
MISSING VALUES CHECKED BEFORE OR AFTER TRANS. .  BEFORE
BLANKS ARE. . . . . . MISSING
INPUT UNIT NUMBER . . . . . .      14
REWIND INPUT UNIT PRIOR TO READING. . DATA. . .     YES
NUMBER OF WORDS OF DYNAMIC STORAGE. . . . . .   14998
NUMBER OF CASES DESCRIBED BY INPUT FORMAT . . .      1

***** TRAN     PARAGRAPH IS USED *****
```

APPENDIX G CONTINUED

EXAMPLE OF RESULTS OF MLR ANALYSIS

```
VARIABLES TO BE USED
     1 SITE        2 DATE        3 MIN         4 JDAY        5 ANGLE
     6 DEV         7 NO3         8 SO4         9 NH4        10 VC
    11 NVC        12 MASS       13 AL         14 SI         15 S
    16 CL         17 K          18 CA         19 TI         20 V
    21 CR         22 MN         23 FE         24 NI         25 CU
    26 ZN         27 SE         28 BR         29 SR         30 ZR
    31 CD         32 SN         33 SB         34 PB         35 NA
    36 NAL        37 SC         38 NV         39 NCR        40 NMN
    41 CO         42 AS         43 NSE        44 MO         45 AG
    46 NCD        47 IN         48 I          49 CS         50 LA
    51 CE         52 SM         53 W          54 AU         55 TH
    56 X50        57 NO3X       58 SO4X       59 NH4X       60 VCX
    61 NVCX       62 MASSX      63 ALX        64 SIX        65 SX
    66 CLX        67 KX         68 CAX        69 TIX        70 VX
    71 CRX        72 MNX        73 FEX        74 NIX        75 CUX
    76 ZNX        77 SEX        78 BRX        79 SRX        80 ZRX
    81 CDX        82 SNX        83 SBX        84 PBX        85 NAX
    86 NALX       87 SCX        88 NVX        89 NCRX       90 NMNX
    91 COX        92 ASX        93 NSEX       94 MOX        95 AGX
    96 NCDX       97 INX        98 IX         99 CSX       100 LAX


PAGE  20  BMDP9R  MASSX VS SX & PBX FOR SITE 28

   101 CEX       102 SMX       103 WX        104 AUX       105 THX
   106 X100      107 DUST      108 OIL       109 PAINT     110 CATCR
   111 INCIN     112 SBROAST   113 ZNDBR     114 VDPB      115 NIDPB
   116 ZNDPB
INPUT FORMAT IS
(6F7.0/10(10F7.0/),10F7.0)
MAXIMUM LENGTH DATA RECORD IS   70 CHARACTERS.

INDEPENDENT VARIABLES ARE
    65 SX         84 PBX

DEPENDENT VARIABLE. . . . . .        62 MASSX
NUMBER OF 'BEST' REGRESSIONS. . . . . .        5
SELECTION CRITERION . . . . . .  NONE
WEIGHT VARIABLE . . . . . .
PRECISION . . . . . .  DOUBLE
TOLERANCE FOR MATRIX INVERSION. . . . . .  .0001000
```

APPENDIX G CONTINUED

EXAMPLE OF RESULTS OF MLR ANALYSIS

DATA AFTER TRANSFORMATIONS

C A S E NO.	LABEL	65 SX	84 PBX	62 MASSX
53		7.785	.197	44.874
54		2.636	.133	15.861
55		1.746	.203	12.150
56		7.821	.232	41.557
57		6.104	.195	37.198

NUMBER OF CASES READ. 157
CASES WITH USE SET TO ZERO 107
REMAINING NUMBER OF CASES 50

SUMMARY STATISTICS FOR EACH VARIABLE

VARIABLE	MEAN	STANDARD DEVIATION	COEF. OF VAR.	SMALLEST VALUE	LARGEST VALUE	SKEW-NESS	KURTOSIS
65 SX	4.08324	2.44498	.598786	.8039	10.58640	.66	-.39
84 PBX	.19548	.10650	.544834	.0679	.60460	1.71	3.14
62 MASSX	26.02734	13.06169	.501845	5.0223	61.08050	.51	-.48

VALUES FOR KURTOSIS GREATER THAN ZERO INDICATE DISTRIBUTIONS
WITH HEAVIER TAILS THAN THE NORMAL DISTRIBUTION.

CORRELATIONS

		SX 65	PBX 84	MASSX 62
SX	65	1.000		
PBX	84	-.008	1.000	
MASSX	62	.957	.149	1.000

STATISTICS FOR 'BEST' SUBSET

SQUARED MULTIPLE CORRELATION	.94081
MULTIPLE CORRELATION	.96996
ADJUSTED SQUARED MULT. CORR.	.93830
RESIDUAL MEAN SQUARE	10.527253
STANDARD ERROR OF EST.	3.244573
F-STATISTIC	373.55
NUMERATOR DEGREES OF FREEDOM	2
DENOMINATOR DEGREES OF FREEDOM	47
SIGNIFICANCE (TAIL PROB.)	.0000

VARIABLE NO.	NAME	REGRESSION COEFFICIENT	STANDARD ERROR	STAND. COEF.	T-STAT.	2TAIL SIG.	TOL-ERANCE	CONTRI-BUTION TO R-SQ
	INTERCEPT	1.35177	1.24272	.103	1.09	.282		
65	SX	5.12007	.189582	.958	27.01	.000	.999933	.91850
84	PBX	19.2816	4.35227	.157	4.43	.000	.999933	.02472

APPENDIX H

PRINTOUT FOR EPA CMB CODE APPLIED TO 30-DAY AVERAGE FINE PARTICLE COMPOSITION AT SITE 28+

```
**********************************************************************************
*                                                                                *
*              U. S. EPA CHEMICAL MASS BALANCE RECEPTOR MODEL                    *
*              *** IBM-PC VERSION 6.0  (REVISED  6/18/87) ***                    *
*                                                                                *
*       EPA PROJECT MGR: THOMPSON G. PACE III, PE                                *
*                        U.S. ENVIRONMENTAL PROTECTION AGENCY                    *
*                        OFFICE OF AIR QUALITY PLANNING AND STANDARDS            *
*                        RESEARCH TRIANGLE PARK, NC                              *
*                        (919)-541-5585                                          *
*                                                                                *
*                                                                                *
*     PRINCIPAL AUTHOR:      DR. JOHN G. WATSON                                  *
*                            DESERT RESEARCH INSTITUTE                           *
*                            UNIVERSITY OF NEVADA SYSTEM                         *
*                            (702)-972-1676                                      *
*                                                                                *
*     CONTRIBUTING AUTHORS:                                                      *
*     DR. J.C. CHOW          MR. P.L. HANRAHAN        DR. N.F. ROBINSON         *
*     MR. J.E. CORE          DR. R.C. HENRY           DR. H.J. WILLIAMSON       *
*     MR. D.A. DUBOSE        MR. T.G. PACE            DR. L. WIJNBERG           *
*                                                                                *
**********************************************************************************
THE "HELP" COMMAND LISTS COMMANDS.
USE COMMANDS AE,DE,AS,DS FOR CHANGES.
ENTER COMMAND
ENTER DESIRED CMB SITE CODE: XXXXXXXXXXXX
ENTER YEAR: YY
ENTER DATE: MMDD
INPUT DESIRED SIZE FRACTION:(FINE OR COARSE)
DATA SEARCH BEGUN FOR
     SITE: Site 28          YEAR: 82  DATE: 0714

     SITE: Site 28          YEAR: 82  DATE: 0714     FC
ENTER COMMAND
SOURCE CONTRIBUTION ESTIMATES -  SITE: Site 28      DATE: 0714 82   VERSION: 6.0
SAMPLE DURATION        30      START HOUR        18        SIZE: FINE
```

+This printout was obtained by running a batch file that contained the command CMB6 < DATA.FIL> SCREEN.OUT
The needed input data were stored in file, DATA.FIL, and results were routed to file, SCREEN.OUT, which was incorporated into the present document.

```
      R SQUARE        .98    PERCENT MASS‡        9.6‡
    CHI SQUARE        .71              DF          7

 SOURCE
 * TYPE      SCE(UG/M3)     STD ERR      TSTAT
-------------------------------------------------
 1 Dust          .9392        .2980     3.1513
 6 Oil-Av        .7028        .1315     5.3452
 8 Paint         .0542        .0413     1.3134
10 CatCr         .2052        .0419     4.8919
11 Incin         .7136        .0710    10.0450
13 SbRoast       .0995        .0116     8.6051
-------------------------------------------------

MEASURED CONCENTRATION FINE/COARSE/TOTAL:
     28.3+-      3.1/      11.4+-      2.8/      39.7+-      4.2
Pause.
Please press <return> to continue.
      UNCERTAINTY/SIMILARITY CLUSTERS  VERSION: 6.0     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------------
       8 10                                                    .259+-      .060
       8 10                                                    .259+-      .060
-------------------------------------------------------------------------------
Pause.
Please press <return> to continue.
SPECIES CONCENTRATIONS -  SITE: Site 28      DATE: 0714 82   VERSION: 6.0
SAMPLE DURATION        30      START HOUR‡       18          SIZE: FINE
      R SQUARE        .98    PERCENT MASS‡        9.6‡
    CHI SQUARE        .71              DF          7

SPECIES-I-M-------MEAS-----------------CALC-------------RATIO C/M----RATIO R/U‡
  1 TOT     28.28200+- 3.12400    2.71454+-   .29649    .10+-  .01 TOT    -8.1‡
  6 SI  *     .10300+-  .02100     .12763+-   .03000   1.24+-  .39 SI       .7‡
  7 S        4.19600+-  .28700     .11586+-   .01252    .03+-  .00 S     -14.2‡
 11 TI  *     .01500+-  .00900     .01708+-   .00167   1.14+-  .69 TI       .2
 14 FE  *     .09100+-  .00700     .07930+-   .02554    .87+-  .29 FE      -.4
 15 NI  *     .01100+-  .00150     .01245+-   .00247   1.13+-  .27 NI       .5
 16 ZN  *     .08200+-  .00600     .08238+-   .00418   1.00+-  .09 ZN       .1
 19 CD  *     .00220+-  .00070     .00096+-   .00106    .44+-  .50 CD     -1.0
 20 SN  *     .00500+-  .00400     .00496+-   .00165    .99+-  .86 SN       .0
 21 SB  *     .07900+-  .00800     .07900+-   .00416   1.00+-  .11 SB       .0‡
 22 PB        .24900+-  .01500     .05469+-   .00956    .22+-  .04 PB    -10.9‡
 24 AL  *     .05300+-  .00600     .04318+-   .01342    .81+-  .27 AL      -.7
 26 V   *     .01300+-  .00140     .01113+-   .00294    .86+-  .24 V       -.6
 33 LA  *    1.12000+-  .12600     .89855+-   .15592    .80+-  .17 LA     -1.1
 34 CE  *     .60900+-  .09700     .75528+-   .15454   1.24+-  .32 CE       .8
 35 SM  *     .04000+-  .00500     .04949+-   .01405   1.24+-  .38 SM       .6
-------------------------------------------------------------------------------
```

‡This CMB accounts for only 9.6% of the measured fine mass because the sulfur-component and vehicle exhaust were excluded. Those components were determined by the composite of CMB and MLR that is explained on page 18. The text on page 18 also explains how the differences between measured and calculated values of S, Pb and mass (TOT) were used as input data for MLR.

APPENDIX I

ANNOTATED PRINTOUTS OF MODEL FOR PARTICULATE EMISSIONS FROM MOTOR VEHICLES

The next two pages show printouts from the model developed by Energy and Environmental Analysis, Inc. for particulate emissions from vehicles[41,42]. The printouts are amended to indicate (**in boldface**) symbols that represent data in certain columns. Also shown (**in boldface**) are Pb emission rates and abundances for a VMT-weighted fleet of vehicles, derived from the model output. Those quantities are defined below.

DERIVED Pb EMISSION RATES AND ABUNDANCES OF Pb IN VMT-WEIGHTED EMISSIONS

VMT-Weighted Emission Rate for Pb

E(Pb) = Σ e(Pb,i) * v(i)/1.557
= Pb emission rate weighted by VMT for all vehicles

e(Pb,i) = PbBrCL emission rate for vehicle class i in <2.5 μm particles

v(i) = fraction of VMT due to vehicle type i

1.557 = factor needed to correct for the fact that the model defines "LEAD" as PbBrCl

VMT-Weighted Emission Rate for Mass

e(mass,i) = Total mass emission rate for vehicle class i in < 2.5 μm particles

E1(mass) = Σ e(tot,i) * v(i)
= Total <2.5 μm particle emission rate for VMT-weighted engine exhaust

E2(mass) = E2(total) + 0.0058 g/mi
= Total <2.5 μm particle emission rate for VMT-weighted engine exhaust, brakes and tires

0.0058 = Emission rate in g/mi for brake and tire wear in <2.5 μm particles

Pb Abundance in VMT-Weighted emissions from vehicles

P1(Pb) = 100 * E(Pb) / E1(mass)
= Percent Pb abundance in VMT-weighted vehicle exhaust

P2(Pb) = 100 * E(Pb) / E2(mass)
= Percent Pb abundance in VMT-weighted emissions that include brake and tire wear

TABLE I1. MODEL RESULTS BASED ON ESTIMATES OF VMT DISTRIBUTION FOR PHILADELPHIA COUNTY

WARNING: VEHICLE SPEED = 35.0 MORE THAN 34.8 MPH FOR SULFATE CAL.
Emissions of <2.5 μm particles for VMT mix characteristic of Phila. County
CALCULATIONS FOR YEAR 1982 SPEED 35.0 MPH PARTICLE CUTOFF = 2.50 MICRONS

FLAG SETTINGS:

TAMPERING RATES	= NORM	MISFUELING RATES	= NORM	VMT MIXTURE	= USER
MILEAGE & REGIST.	= NORM	I/M PROGRAM	= YES	SPECIAL CONDITIONS	= NORM
DRIVING CONDITIONS	= CRSE				

PARTICULATE EMISSIONS (GRAMS/MILE) BY VEHICLE CLASS

	e(Pb,i)				e(mass,i)	v(i)	e(mass,i)*v(i)
VEH.CLASS	LEAD	ORGANIC	SULFATE	DIESEL	TOTAL	VMT FRAC.	VMT WT. TOT
LDV	.0113	.0230	.0070	.0087	.0499	.7565	.0377
LDT1	.0166	.0264	.0052	.0094	.0576	.0800	.0046
LDT2	.0338	.0247	.0039	.0094	.0718	.0450	.0032
HDGV	.0825	.1054	.0017	.0000	.1896	.0500	.0095
HDDT	.0000	.0000	.0000	1.9171	1.9171	.0600	.1150
MC	.0304	.0000	.0000	.0000	.0304	.0085	.0003

TOTAL BRAKE PARTICULATES = .0053
TOTAL TIRE PARTICULATES = .0005
TOTAL VMT WEIGHTED PARTICULATE EMISSIONS = .1762 = **E2(mass)**

PARTICULATE FRACTION BY VEHICLE CLASS

VEH.CLASS	LEAD	ORGANIC	SULFATE	DIESEL
LDV	.2264	.4603	.1396	.1737
LDT1	.2877	.4581	.0908	.1635
LDT2	.4701	.3439	.0548	.1311
HDGV	.4351	.5559	.0090	.0000
HDDT	.0000	.0000	.0000	1.0000
MC	1.0000	.0000	.0000	.0000

E(Pb) = 0.0101 g/mi

E1(mass) = 0.1704 g/mi
E2(mass) = 0.1762 g/mi

P1(Pb) = 5.95%
P2(Pb) = 5.75%

TABLE I2. MODEL RESULTS FOR TURNPIKE VMT DISTRIBUTION

WARNING: VEHICLE SPEED = 55.0 MORE THAN 34.8 MPH FOR SULFATE CAL.
Model Results for Turnpike VMT Distribution

CALCULATIONS FOR YEAR 1982 SPEED 55.0 MPH PARTICLE CUTOFF = 2.50 MICRONS

FLAG SETTINGS:
TAMPERING RATES = NORM MISFUELING RATES = NORM VMT MIXTURE = USER
MILEAGE & REGIST. = NORM I/M PROGRAM = YES SPECIAL CONDITIONS = NORM
DRIVING CONDITIONS = CRSE

PARTICULATE EMISSIONS (GRAMS/MILE) BY VEHICLE CLASS

	e(Pb,i)				e(mass,i)	v(i)	e(mass,i)*v(i)
VEH.CLASS	LEAD	ORGANIC	SULFATE	DIESEL	TOTAL	VMT FRAC.	VMT WT.
TOT							
LDV	.0127	.0230	.0082	.0087	.0526	.6855	.0360
LDT1	.0186	.0264	.0058	.0094	.0602	.0800	.0048
LDT2	.0380	.0247	.0042	.0094	.0763	.0450	.0034
HDGV	.0825	.1054	.0017	.0000	.1896	.0240	.0046
HDDT	.0000	.0000	.0000	1.9171	1.9171	.1570	.3010
MC	.0304	.0000	.0000	.0000	.0304	.0085	.0003

TOTAL BRAKE PARTICULATES = .0053
TOTAL TIRE PARTICULATES = .0005
TOTAL VMT WEIGHTED PARTICULATE EMISSIONS = .3559 = **E2(mass)**

PARTICULATE FRACTION BY VEHICLE CLASS

VEH.CLASS	LEAD	ORGANIC	SULFATE	DIESEL
LDV	.2415	.4368	.1568	.1648
LDT1	.3093	.4382	.0962	.1563
LDT2	.4974	.3237	.0555	.1234
HDGV	.4351	.5559	.0090	.0000
HDDT	.0000	.0000	.0000	1.0000
MC	1.0000	.0000	.0000	.0000

E(Pb) = 0.0091 g/mi

E1(mass) = 0.3501 g/mi
E2(mass) = 0.3559 g/mi

P1(Pb) = 2.59%
P2(Pb) = 2.55%